



Subject: FW: Focusing WIPP's Current Committee on the Science Behind Optimizing TRU Waste Analyses

From: "Pastina, Barbara" <bpastina@nas.edu>

Date: Mon, 22 Sep 2003 14:23:44 -0400

To: <Steve_Zappe@nmenv.state.nm.us>

-----Original Message-----

From: Nelson, Roger - DOE [<mailto:Roger.Nelson@wipp.ws>]

Sent: Tuesday, September 09, 2003 5:45 PM

To: Pastina, Barbara

Subject: FW: Focusing WIPP's Current Committee on the Science Behind Optimizing TRU Waste Analyses

Barbara:

I am forwarding this without any attachments to see if its the size of the e-mail that is causing you not to be able to access it remotely.....Roger

Please call if you receive this e-mail.....505.234.7213.....Roger

-----Original Message-----

From: Nelson, Roger - DOE

Sent: Tuesday, September 09, 2003 3:06 PM

To: 'bpastina@nas.edu'

Subject: FW: Focusing WIPP's Current Committee on the Science Behind Optimizing TRU Waste Analyses

Barbara:

I am forwarding Ines Triay's e-mail to you again. Her original e-mail included 5 attachments. One of them was a 10MB file (lots of graphics), and

maybe that was why her e-mail didn't come through. This e-mail forwards hers but I cut out the large file.....Roger

-----Original Message-----

From: Renfrow, Julie - DOE On Behalf Of Triay, Ines - DOE

Sent: Monday, September 08, 2003 9:16 AM

To: 'kcrowley@nas.edu'

Cc: 'bpastina@nas.edu'; 'ahearne@sigmaxi.org'; Silva, Matthew - EEG; Nelson, Roger - DOE

Subject: Focusing WIPP's Current Committee on the Science Behind Optimizing TRU Waste Analyses

Dr. Kevin Crowley, Staff Director
Board on Radioactive Waste Management
The National Academies
500 5th Street, NW, 6th Floor
Washington, DC 20001

Subject: Focusing WIPP's Current Committee on the Science Behind Optimizing TRU Waste Analyses

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Dear Kevin

The U.S. Department of Energy has long enjoyed review and scientific advice from the National Academies. Over the past decade as WIPP evolved through difficult controversy, DOE has rigorously followed the recommendations made by the various NAS Committees on WIPP. That advice has served DOE well in furthering the safe and cost effective design, and now operation, of the nation's only deep geologic repository for disposal of radioactive waste. Following the completion of the work of the NAS Committee for "Improving Operations and Long Term Safety of WIPP" in 2001, Congress even directed DOE

to heed their recommendations in the Energy and Water Appropriations Bill language for 2002. Since then, DOE has diligently collected even more information on the future waste inventory and tirelessly appealed to its regulatory authorities for reduction in unnecessary characterization requirements. DOE even requested NAS to form yet a third Committee to make even stronger recommendations on "Optimizing the Characterization and Transportation of Transuranic Waste Destined for WIPP".

I believe the recent public debate over NAS agreement with Senate Bill 1424, Section 310 may have politicized the current Committee's deliberations. At the very least, these discussions may have detracted from the new Committee's focus on the additional data that we have collected to support the following recommendation made by the previous Committee:

"The committee recommends that the DOE's effort to review waste characterization and packaging requirements continue and that changes be implemented over the entire National TRU Program.", Improving Operations and

Long-Term Safety of the WIPP Final Report, NRC, 2001, pgs. 33-3

Therefore, I would like to bring the current Committee's focus back to the realities of the scientific arguments. I have attached five technical papers that describe the scientific arguments for making changes equivalent to those that would be effected if the legislation were enacted today. We intend to publish all of these arguments in the refereed literature in the near future. While we have made these same arguments qualitatively to the current Committee over the last year, we believe they should consider these more quantitative versions as they draft their report conclusions. Therefore, we respectfully request that these materials be forwarded to the current committee as soon as possible.

1. Analysis of Volatile Organic Compound Levels in the Transuranic Waste Inventory
2. Statistical Analysis of Volatile Organic Compound Levels in Transuranic Waste
3. Technical Evaluation Report for WIPP Room-Based VOC Monitoring
4. An Analysis of TRU Waste Characterization Accuracy
5. Statutory, Regulatory and Guidance Justification for Changing Mixed Waste Analysis Requirements at the Waste Isolation Pilot Plant

If you or the Committee members have any questions about the accompanying analyses, please allow me and my staff an opportunity to provide answers in advance of the Committee's draft report.

Sincerely,

Ines Triay, Ph.D.
Manager

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**Analysis of Volatile Organic Compound Levels
in the Transuranic Waste Inventory**

William H. McCulla and Gregory D. Van Soest, LANL-EES-12
September 4, 2003

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Executive Summary

A previous assessment of volatile organic compounds (VOCs) in transuranic (TRU) waste was performed by the Idaho National Engineering and Environmental Laboratory (INEEL) in 1995 in support of the Waste Isolation Pilot Plant (WIPP) Resource Conservation and Recovery Act (RCRA) Part B Permit Application (1). That analysis was conducted on 930 drums of TRU mixed waste that originated only from INEEL and the Rocky Flats Environmental Technology Site (RFETS). The results of that analysis were the weighted average values for each of 28 VOCs.

It is important to note that most of the final waste forms (FWFs) (previously designated, Waste Matrix Code Groups) were represented by less than 100 headspace gas data points. With so few total data points, it is reasonable to re-evaluate the conclusions reached earlier regarding expected VOC levels in the WIPP repository.

A new assessment of VOC levels in TRU waste using all known currently available VOC data is the subject of this report. A waste inventory update was performed for the DOE Complex in 2003 in support of the WIPP Performance Re-certification Application (2). That inventory information is the best basis upon which to project the expected VOC contributions by FWFs from the waste that will be contained in a full WIPP repository.

Using updated data and a much larger population of headspace gas samplings, a new weighted average VOC source term for 28 VOCs has been determined. The principal VOCs contributing to the new source term have been reduced from three in the 1995 data to two in the new data set. These are 1,1,1-trichloroethane and carbon tetrachloride. The FWFs that are principal contributors to the VOC source term have been reduced from three in the 1995 data to one in the new data set. This FWF is solidified organics. The weighted-average source term for the two principal VOC contributors in the new data set -- 1,1,1-trichloroethane and carbon tetrachloride -- have decreased to 38 percent and 41 percent respectively of their 1995 values.

A breakdown by site for the principal FWF VOC contributor, solidified organics, has been completed and the 2003 Inventory Update (2) indicates that only four sites contain the bulk of the problem. The large sites are RFETS, INEEL, Los Alamos National Laboratory (LANL), and the Hanford Reservation, with the Energy Technology Center (ETEC) and Lawrence Livermore National Laboratory (LLNL) having only about 13 m³ total.

According to the 2003 Inventory Update, all the solidified organic FWFs at INEEL originated at RFETS, primarily as VOC-contaminated solidified oils. Thus all the solidified organics headspace gas data in this survey effectively was obtained from RFETS waste and only represents the FWF VOC levels for that facility. This assessment, then, may not accurately represent the average VOC levels for solidified organic FWFs for the Department of Energy (DOE) Complex.

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Currently, no headspace gas data are available for solidified organics for LANL or Hanford. The 2003 Inventory Update estimates there are less than 2,000 m³ -- both stored and projected -- of solidified organics in the DOE Complex. RFETS and INEEL represent less than one-third of the total.

Even conservative acceptance of the current data as representative of all solidified organic FWFs for the DOE Complex creates no threat of exceeding WIPP emission standards. This conclusion can be made apart from any further headspace gas sampling. The anticipated volume of solidified FWFs is not sufficiently large to result in a threat to either room-based limits or WIPP emission limits for an open room.

Analysis of VOC Levels in the TRU Waste Inventory

William H. McCulla and Gregory D. Van Soest, LANL-EES-12

A previous assessment of VOCs in TRU waste was performed by INEEL in 1995 in support of the WIPP RCRA Part B Permit Application (1). That analysis was conducted on 930 drums of TRU mixed waste that originated only from INEEL and RFETS.

The results of that analysis are presented in Table 1 as the weighted-average values for each of 28 VOCs. The weighting factors are determined by dividing the scaled volume for a final waste form (FWF) by the total WIPP volume and are presented in Table 2. It is important to note that most of the FWFs were represented by less than 100 headspace gas data points (Figure 1). With so few total data points, it is reasonable to re-evaluate the conclusions that were reached earlier regarding expected VOC levels in the WIPP repository.

Since 1995, much more VOC data has been generated which allows for an analysis which includes many more relevant data points. A new assessment of VOC levels in TRU waste using all known currently available VOC data is the subject of this report.

Table 1 1995 Calculation
WEIGHTED AVERAGE CONCENTRATIONS OF HEADSPACE GASES

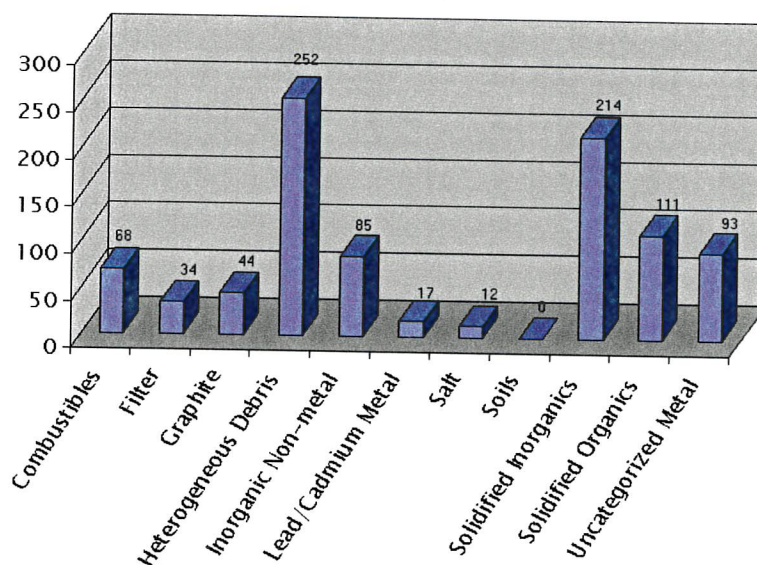
<u>Constituent</u>	<u>Weighted Average (ppmv)</u>
1,1,1-Trichloroethane	3.17E+02
1,1,2,2-tetrachloroethane	9.35E+00
1,1,2-Trichloro-1,2,2-trifluoroethane	3.30E+01
1,1-Dichloroethane	1.02E+01
1,1-Dichloroethylene	1.15E+01
1,2,4-Trimethylbenzene	1.22E+01
1,2-Dichloroethane	9.07E+00
1,3,5-Trimethylbenzene	8.62E+00
Butanol	7.81E+01
Methyl ethyl ketone	6.37E+01
Methyl isobutyl ketone	7.90E+01
Acetone	7.98E+01
Benzene	9.25E+00
Bromoform	9.38E+00
Carbon tetrachloride	3.86E+02
Chlorobenzene	1.25E+01
Chloroform	2.53E+01
(cis)-1,2-Dichloroethylene	8.97E+00
Cyclohexane	2.75E+01
Ethyl benzene	1.16E+01
Ethyl ether	1.33E+01
Methanol	2.13E+02
Methylene Chloride	3.68E+02
o-Xylene	1.60E+01
p/m-Xylene	1.93E+01
Tetrachloroethylene	9.40E+00
Toluene	1.94E+01
Trichloroethylene	2.51E+01

Table 2 1995 Calculation
TRU Waste Disposal Inventory and Weighting Factors for Weighting Average Calculation

Final Waste Form	Stored Volume, m ³	Projected Volume, m ³	Scaled Volume, m ³	Weighting Factor
Combustibles	7.10E+03	2.70E+04	6.20E+04	3.53E-01
Filter	4.30E+02	1.10E+03	2.60E+03	1.48E-02
Graphite	6.70E+02	4.30E+01	7.60E+02	4.30E-03
Heterogeneous	3.00E+04	4.60E+03	3.90E+04	2.22E-01
Inorganic non-metal	1.20E+03	3.20E+02	1.80E+03	1.02E-02
Lead/Cadmium metal	5.60E+01	1.30E+02	3.10E+02	1.80E-03
Salt Waste	3.30E+01	6.00E+01	1.50E+02	8.52E-04
Soils	3.70E+02	4.50E+02	1.30E+03	7.39E-03
Solidified inorganics	1.70E+04	8.00E+03	3.40E+04	1.94E-01
Solidified organics	1.50E+03	3.00E+02	2.10E+03	1.20E-02
Uncategorized metal	1.20E+04	8.60E+03	3.00E+04	1.71E-01
Unknown	1.70E+03	0.00E+00	1.70E+03	9.66E-03
Total	7.21E+04	5.06E+04	1.76E+05	1.00E+00

Weighting factors were determined by dividing scaled volume for each waste matrix code group by the total scaled volume

Figure 1. Containers by Final Waste Form, 1995 Data



A Waste Inventory Update was performed for the DOE Complex in 2003 in support of the WIPP Performance Re-certification Application (2). That inventory information is the best basis upon which to project the expected VOC contributions by FWFs from the waste that will be contained in a full WIPP repository. The waste stream volume information in the 2003 Inventory Update was scaled to a full WIPP by adjusting the projected waste stream volumes such that the sum of all stored volumes and scaled projected volumes equaled the full WIPP volume. The resultant volume data from the 2003 Inventory Update were broken out by FWF and the ratio of the volume of an FWF to the total WIPP volume was determined for each

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FWF. That ratio is used as the weighting factor in this new source term determination for VOCs. The results of this analysis are provided in Table 3.

**Table 3 2003 Calculation
TRU Waste Final Waste Forms and Weighting
Factors for Weighting Average Calculation**

Contact-Handled Waste				
Final Waste Form	Stored Volumes	Projected Volumes	Scaled Volumes	Weighting Factor
Combustible	4.87E+03	1.92E+03	8.91E+03	5.29E-02
Filter	1.33E+03	5.90E+02	2.57E+03	1.53E-02
Graphite	1.24E+02	1.25E+00	1.26E+02	7.51E-04
Heterogeneous Debris	4.95E+04	9.71E+03	7.00E+04	4.15E-01
Inorganic Non-Metal	1.22E+04	6.77E+01	1.23E+04	7.31E-02
Lead/Cadmium Metal	2.24E+02	3.23E+01	2.92E+02	1.73E-03
Salt	1.65E+03	1.86E+02	2.04E+03	1.21E-02
Soils	2.98E+02	6.03E+03	1.30E+04	7.73E-02
Solidified Inorganics	4.20E+04	7.28E+02	4.36E+04	2.59E-01
Solidified Organics	1.33E+03	3.75E+02	2.12E+03	1.26E-02
Uncategorized Metal	2.76E+03	5.11E+03	1.35E+04	8.04E-02
TOTAL	1.16E+05	2.48E+04	1.68E+05	1.00E+00

For the current analysis, a database that contains both old and current headspace gas data for VOCs within the DOE Complex was generated using Microsoft Access. The database contains VOC data from the following resources:

- WIPP Waste Information System (WWIS) data ranging from March 1999 to May 2003 (3)
- The 930-drum data set originally used in the VOC analysis for the WIPP Part B Permit Application (1)
- Data derived from 2,366 drums in an IT Corporation survey for Westinghouse TRU Solutions; study of VOCs in drums at RFETS that could impact hydrogen-getters through poisoning by VOCs (4)
- Study of 103 drums of IDC 003 RFETS waste at INEEL, analyzed to determine hydrogen and flammable VOC content for shipment of this waste to WIPP (5).

The database was modified before weighted averages were calculated by applying the following screening factors. The screening factors numbers two and three reflect current requirements for WIPP compliant waste. These requirements were not in place in 1996:

1. All waste information without an FWF assignment was assigned an FWF using the Waste Matrix Code and Table 1-2 of Reference 6. Two drums in the 930-drum data set used in the VOC analysis for the WIPP RCRA Part B Permit were found to have conflicting FWFs and WMCs. Upon further investigation, it was determined that the WMC assignment was correct and the FWF was changed.

2. The TRAMPAC Revision 19 method was used to determine whether a drum exceeded the mixture lower flammability limit (MLFL) for VOCs and hydrogen (7). This was applied to individual drum data from all sources except WWIS. All drums that failed the MLFL screening were eliminated from further consideration since they would not pass the shipping criteria. The data in WWIS had already been screened for flammability limits and was therefore not screened again.
3. The time for a VOC within a drum's headspace to reach equilibrium with the surrounding outside air through a Nuclear Filter Technologies Inc. NFT-013 filter was calculated (8). The diffusivity values for the calculation were taken from reference 9. Approximately 90 percent of equilibrium was reached in 30 days for the VOC, carbon tetrachloride. Since diffusivity values for the nine VOCs of concern in WIPP differ only by approximately 20 percent (9), the 30-day period to 90 percent of equilibrium was assumed for all VOCs. All data except that from WWIS were screened for drum vent date and drum sampling date. Drums that were sampled less than 30 days after venting were eliminated from the data set since their VOC levels were not near equilibrium, a condition required of all drums emplaced in WIPP.
4. Since multiple data sets that potentially contained the same drum information were used, data were screened for duplicate entries and only the latest entry with the most recent date was retained.
5. The data qualifier for each measurement was included in the imported data. If the qualifier was "U," the qualifier for measurements at or below the method detection limit, one-half the reported value was used for the concentration in calculating the weighted average.
6. All "B"-qualified data were eliminated from the data field because that qualifier is used for contamination observed in the blank and indicates a suspect measurement.

The screening process described above was first applied to the original 930-drum population used in 1995 to determine the effect on the VOC source term of removing drums that could not be shipped to WIPP. Of the 930 samples in the original population, 130 were removed based on the above screening process. Table 4 displays the results of this analysis and shows the effect of the screening criteria. A comparison of these results with those from the earlier study shows the weighted average for the carbon tetrachloride source term decreased from 386 ppmv to 253 ppmv. Screening factors two and three had the largest effect on the change in weighted average. Screening factors five and six have virtually no effect on weighted averages.

Table 4 2003 Calculation on 930 drum data set
Comparison of 1995 data for carbon tetrachloride without and with screening factors.

	Before Screening		After Screening	
	Number of drums in population	Weighted concentration ppmv	Number of drums in population	Weighted concentration ppmv
Combustible	68	200.02	67	183
Filter	34	0.02	30	0.02
Graphite	44	0	43	0
Heterogeneous Debris	252	21.72	221	23.32
Inorganic Non-Metal	85	0.03	80	0.02
Lead/Cadmium Metal	17	0.46	14	0.19
Salt	12	0	12	0
Soils	0	0	0	0
Solidified Inorganics	214	61.41	176	1.9
Solidified Organics	111	99.84	72	44.39
Uncategorized Metal	93	2.83	85	0.065
Total	930	386.33	800	252.905

The four data sets listed on page 6 represent the headspace gas data available in May 2003 and include the original 930-drum data set. To obtain a 2003 assessment of VOC levels expected in WIPP, the four data sets were screened (with exceptions as noted above for WWIS data) to remove non-shippable drums, sorted by FWF, and each VOC was summed within an FWF. The mean was then calculated for each VOC. The total number of drums for all FWFs in the analysis was 45,491. The sample population distribution by source and by FWF is shown in Figure 2. Results of the analysis are provided in Table 5 for each reported VOC.

The mean value for all FWFs has decreased when compared to the 1995 results, with the exception of the solidified organics FWF as shown in Figure 1a. The mean value has remained in the hundreds of ppmv for all VOCs except for the solidified organics FWF. For the solidified organics FWF, the most significant difference is that mean values for 1,1,1-trichloroethane and carbon tetrachloride have increased by 90 percent and 62 percent (respectively) compared to the 1995 results.

The new weighting factor for each FWF listed in Table 3 and mean concentration values for each VOC in each FWF in Table 5 were multiplied together to obtain a weighted VOC concentration by FWF. The weighted concentration values for a given VOC were summed for each FWF to obtain a source term for each of the 28 VOCs. Those results are presented graphically in Figure 3 and displayed in Table 6.

Finally, the weighted source terms for all 28 VOCs are compared for the 1995 data analysis and the new 2003 data analysis in Figure 4.

Figure 1a
Sum of Averages of 28 VOCs by FWF (PPMV)

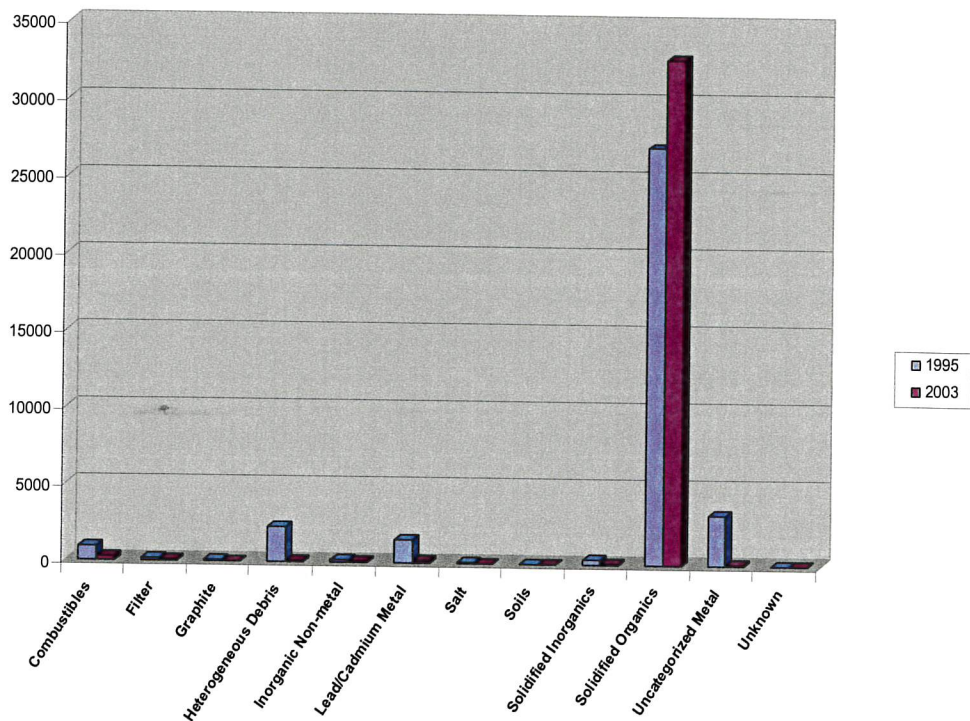
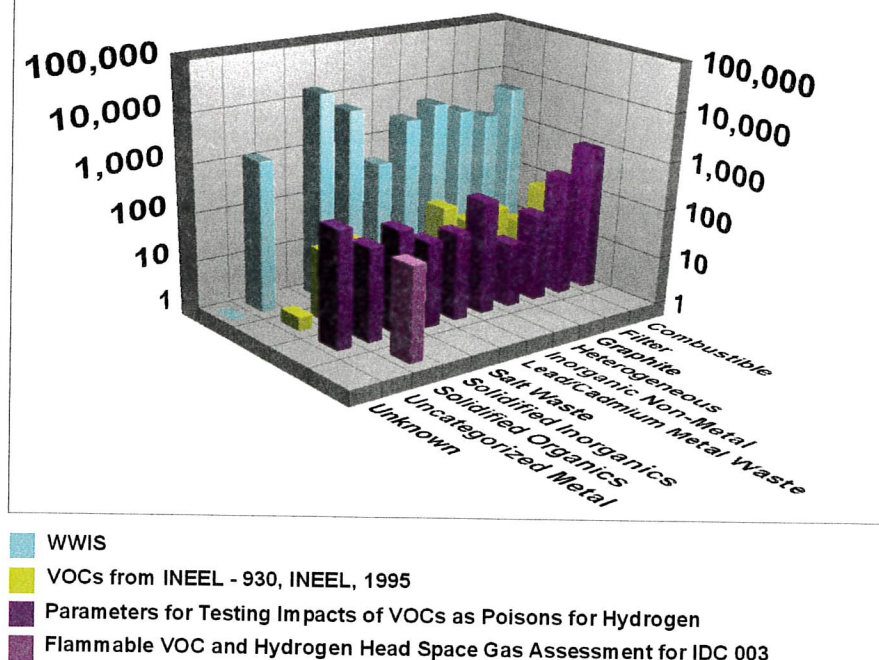


Fig. 2 Sample Population Distribution by Source & Final Waste Form



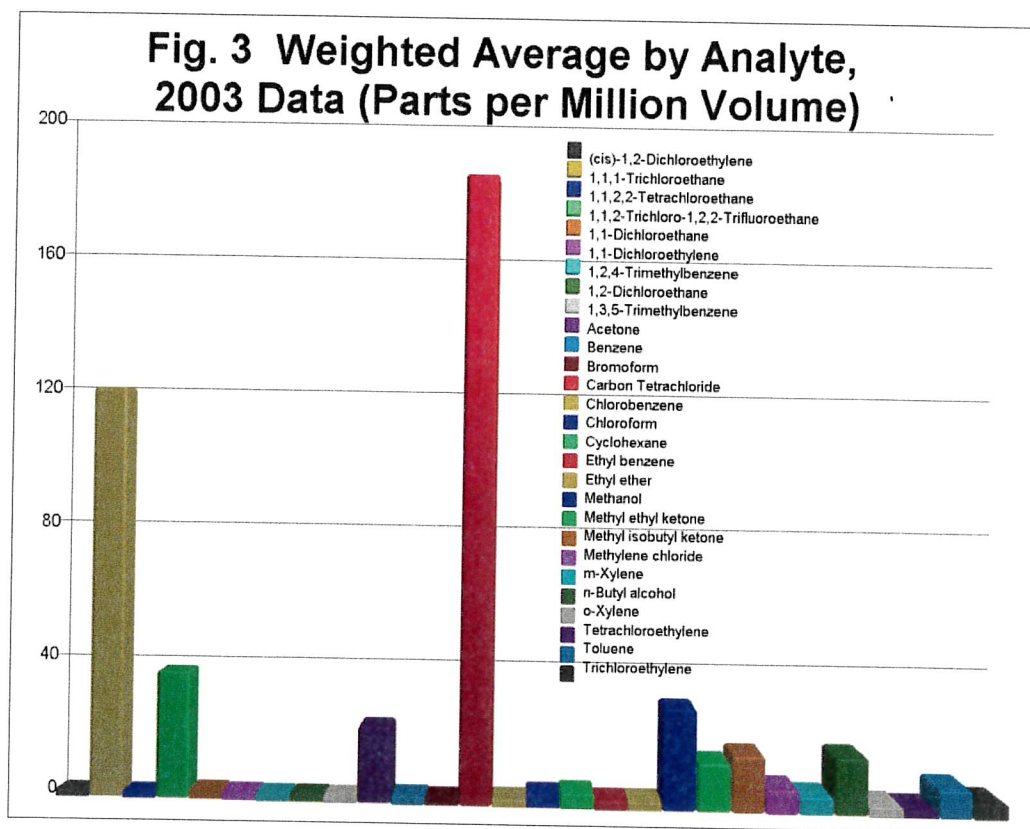


Fig. 4 Comparison of Weighted Averages (PPMV) by Analyte, 1995 and 2003 data

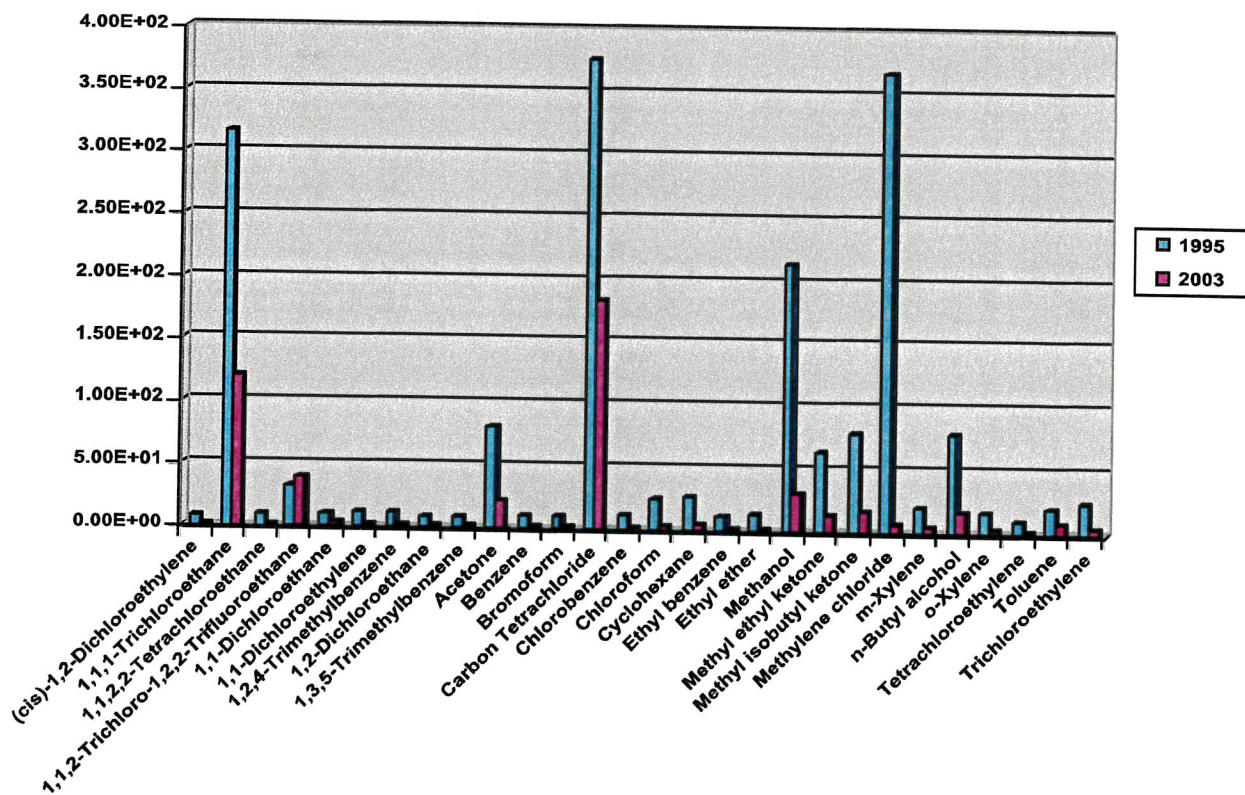


Table 5 Average Values for 28 VOCs

Average/Mean PPMV

Final Waste Form	(cis)-1,2-Dichloroethylene	1,1,1-Trichloroethane	1,1,2,2-Tetrachloroethane	1,1,2-Trichloro-1,2,2-trifluoroethane	1,1-Dichloroethane	1,1-Dichloroethylene	1,2,4-Trimethylbenzene	1,2-Dichloroethane	1,3,5-Trimethylbenzene	Acetone	Benzene	Bromoform	Carbon tetrachloride	Chlorobenzene
Combustible	1.14E+00	9.03E+01	1.10E+00	1.03E+01	1.26E+00	1.62E+00	1.02E+00	1.11E+00	9.25E-01	1.73E+01	1.58E+00	1.05E+00	6.10E+01	1.20E+00
Filter	2.57E-01	1.17E+01	2.41E-01	1.68E+01	5.91E-01	4.46E-01	2.76E-01	3.46E-01	2.54E-01	1.93E+01	1.08E+00	2.71E-01	4.53E+00	2.49E-01
Graphite	2.39E-01	8.13E+00	2.44E-01	3.24E-01	2.94E-01	3.57E-01	2.33E-01	2.60E-01	2.08E-01	8.12E+00	6.17E-01	2.23E-01	6.00E-01	2.04E-01
Heterogeneous	9.12E-01	3.72E+00	9.03E-01	9.82E-01	8.82E-01	8.44E-01	7.94E-01	8.97E-01	7.67E-01	1.10E+01	1.10E+00	8.25E-01	1.18E+00	8.88E-01
Inorganic Non-Metal	2.28E-01	1.61E+01	2.26E-01	2.41E-01	4.07E-01	3.32E-01	2.35E-01	2.75E-01	2.26E-01	7.54E+00	3.53E-01	2.07E-01	2.57E+00	2.20E-01
Lead/Cadmium Metal Waste	2.57E-01	7.65E+01	3.07E-01	1.07E+00	7.76E-01	6.70E-01	3.18E-01	2.84E-01	2.61E-01	1.62E+01	4.89E-01	2.24E-01	2.41E+01	2.60E-01
Salt Waste	2.61E-01	2.70E-01	2.61E-01	2.65E-01	4.95E-01	2.66E-01	2.59E-01	2.62E-01	2.58E-01	3.19E+00	5.85E-01	2.60E-01	2.71E-01	2.58E-01
Solidified Inorganics	2.47E-01	2.90E+01	2.14E-01	6.20E+00	7.77E-01	1.09E+00	2.34E-01	2.32E-01	2.13E-01	3.94E+00	7.34E-01	2.06E-01	1.45E+00	2.06E-01
Solidified Organics	1.23E+02	8.34E+03	1.08E+02	2.73E+03	1.53E+02	1.27E+02	1.16E+02	1.11E+02	1.00E+02	1.07E+03	1.13E+02	1.05E+02	1.41E+04	1.14E+02
Uncategorized Metal	6.26E-01	3.61E+00	6.46E-01	8.68E-01	6.02E-01	6.71E-01	7.29E-01	6.67E-01	7.18E-01	1.76E+01	1.83E+00	7.09E-01	1.87E+00	6.13E-01
Unknown	2.50E-01	2.50E-01	2.50E-01	2.50E-01	2.50E-01	2.50E-01		2.50E-01		7.40E+00	7.30E-01	2.50E-01	2.50E-01	2.50E-01

(Table 5 continued) Final Waste Form	Chloroform	Cyclohexane	Ethyl benzene	Ethyl ether	Methanol	Methyl ethyl ketone	Methyl isobutyl ketone	Methylene chloride	m-Xylene	n-Butyl alcohol	o-Xylene	Tetrachloroethylene	Toluene	Trichloroethylene
Combustible	6.09E+00	5.08E+00	1.99E+00	1.24E+00	2.43E+01	7.90E+00	9.21E+00	2.49E+01	4.65E+00	1.51E+01	2.37E+00	1.26E+00	7.28E+00	4.70E+00
Filter	1.10E+00	3.29E-01	4.06E-01	3.26E-01	1.77E+01	4.47E+00	3.73E+00	7.44E+00	1.22E+00	2.72E+00	5.52E-01	3.16E-01	6.39E+00	1.60E+00
Graphite	3.70E-01	2.47E-01	2.58E-01	3.15E-01	1.03E+01	2.34E+00	2.27E+00	6.99E-01	3.93E-01	3.38E+00	2.39E-01	2.19E-01	2.13E+00	4.80E-01
Heterogeneous	9.57E-01	8.63E-01	1.10E+00	9.23E-01	1.53E+01	7.60E+00	1.01E+01	4.27E+00	2.70E+00	7.86E+00	1.29E+00	9.20E-01	7.18E+00	1.07E+00
Inorganic Non-Metal	1.62E+00	1.31E+01	2.58E-01	3.10E-01	1.49E+01	2.52E+00	1.73E+00	1.18E+00	4.14E-01	3.68E+00	2.58E-01	2.31E-01	7.35E+00	2.50E+00
Lead/Cadmium Metal Waste	1.85E+00	3.72E-01	4.24E-01	3.76E-01	6.70E+00	6.74E+00	9.75E-01	1.82E+00	5.52E-01	2.29E+00	3.50E-01	2.65E-01	1.52E+01	9.86E+00
Salt Waste	3.06E-01	2.62E-01	2.62E-01	7.40E-01	1.29E+01	2.61E+00	2.37E+00	5.03E-01	3.26E-01	7.24E+00	2.60E-01	2.59E-01	1.38E+00	4.93E-01
Solidified Inorganics	2.61E-01	4.36E-01	4.55E-01	4.47E-01	1.25E+01	1.75E+00	1.49E+00	2.23E+00	1.05E+00	4.18E+00	3.22E-01	9.60E-01	3.84E+00	3.69E+00
Solidified Organics	2.10E+02	2.03E+02	1.16E+02	1.30E+02	1.26E+03	7.21E+02	7.96E+02	2.36E+02	1.47E+02	8.30E+02	1.47E+02	1.07E+02	1.76E+02	1.92E+02
Uncategorized Metal	7.28E-01	6.30E-01	2.00E+00	6.81E-01	1.50E+01	7.16E+00	1.43E+01	1.96E+00	6.59E+00	6.99E+00	2.14E+00	7.08E-01	1.05E+01	1.02E+00
Unknown	2.50E-01		2.50E-01	2.50E-01	5.50E+00	2.55E+00	1.85E+00	1.09E+00	5.00E-01	2.50E+00	2.50E-01	2.50E-01	8.50E-01	2.50E-01

Table 6 Weighted Average for 28 VOCs

Weighted Average PPMV

Final Waste Form	(cis)-1,2-Dichloroethylene	1,1,1-Trichloroethane	1,1,2,2-Tetrachloroethane	1,1,2-Trichloro-1,2,2-trifluoroethane	1,1-Dichloroethane	1,1-Dichloroethylene	1,2,4-Trimethylbenzene	1,2-Dichloroethane	1,3,5-Trimethylbenzene	Acetone	Benzene	Bromoform	Carbon tetrachloride	Chlorobenzene
Combustible	6.05E-02	4.25E+00	5.83E-02	5.43E-01	6.69E-02	8.57E-02	5.42E-02	5.87E-02	4.90E-02	9.16E-01	8.38E-02	5.56E-02	3.23E+00	6.37E-02
Filter	3.93E-03	1.79E-01	3.69E-03	2.57E-01	9.04E-03	6.83E-03	4.22E-03	5.29E-03	3.88E-03	2.96E-01	1.65E-02	4.14E-03	8.94E-02	3.82E-03
Graphite	1.80E-04	6.11E-03	1.83E-04	2.44E-04	2.21E-04	2.68E-04	1.75E-04	1.95E-04	1.56E-04	6.10E-03	4.63E-04	1.67E-04	4.51E-04	1.53E-04
Heterogeneous	3.78E-01	1.54E+00	3.75E-01	4.08E-01	3.66E-01	3.50E-01	3.30E-01	3.72E-01	3.18E-01	4.58E+00	4.55E-01	3.42E-01	4.88E-01	3.69E-01
Inorganic Non-Metal	1.66E-02	1.17E+00	1.65E-02	1.76E-02	2.98E-02	2.43E-02	1.72E-02	2.01E-02	1.65E-02	5.51E-01	2.58E-02	1.51E-02	1.88E-01	1.61E-02
Lead/Cadmium Metal Waste	4.45E-04	1.32E-01	5.31E-04	1.84E-03	1.34E-03	1.16E-03	5.51E-04	4.91E-04	4.51E-04	2.81E-02	3.46E-04	3.87E-04	4.17E-02	4.49E-04
Salt Waste	3.15E-03	3.27E-03	3.15E-03	3.21E-03	5.99E-03	3.22E-03	3.13E-03	3.17E-03	3.12E-03	3.86E-02	7.07E-03	3.14E-03	3.28E-03	3.12E-03
Solidified Inorganics	6.39E-02	7.51E+00	5.55E-02	1.61E+00	2.01E-01	2.81E-01	6.07E-02	6.00E-02	5.53E-02	1.02E+00	1.90E-01	5.34E-02	3.76E-01	5.34E-02
Solidified Organics	1.55E+00	1.06E+02	1.36E+00	3.44E+01	1.92E+00	1.60E+00	1.46E+00	1.39E+00	1.27E+00	1.35E+01	1.43E+00	1.32E+00	1.78E+02	1.43E+00
Uncategorized Metal	5.03E-02	2.90E-01	5.20E-02	8.98E-02	4.84E-02	5.39E-02	5.86E-02	5.36E-02	5.77E-02	1.42E+00	1.47E-01	5.70E-02	1.50E-01	4.93E-02
Unknown														

Table 6 Continued) Final Waste Form	Chloroform	Cyclohexane	Ethyl benzene	Ethyl ether	Methanol	Methyl ethyl ketone	Methyl isobutyl ketone	Methylene chloride	m-Xylene	n-Butyl alcohol	o-Xylene	Tetrachloroethylene	Toluene	Trichloroethylene
Combustible	3.22E-01	2.69E-01	1.05E-01	6.56E-02	1.29E+00	4.18E-01	4.87E-01	1.32E+00	2.46E-01	8.00E-01	1.25E-01	6.67E-02	3.85E-01	2.49E-01
Filter	1.68E-02	5.03E-03	6.21E-03	4.98E-03	2.70E-01	6.83E-02	5.71E-02	1.14E-01	1.86E-02	4.16E-02	8.45E-03	4.83E-03	9.78E-02	2.45E-02
Graphite	2.78E-04	1.86E-04	1.94E-04	2.37E-04	7.73E-03	1.76E-03	1.71E-03	5.25E-04	2.95E-04	2.53E-03	1.79E-04	1.65E-04	1.60E-03	3.60E-04
Heterogeneous	3.97E-01	3.58E-01	4.58E-01	3.83E-01	6.34E+00	3.16E+00	4.18E+00	1.77E+00	1.12E+00	3.26E+00	5.34E-01	3.82E-01	2.98E+00	4.43E-01
Inorganic Non-Metal	1.11E-01	9.55E-01	1.89E-02	2.27E-02	1.09E+00	1.84E-01	1.27E-01	8.63E-02	3.03E-02	2.62E-01	1.88E-02	1.69E-02	5.37E-01	1.82E-01
Lead/Cadmium Metal Waste	3.20E-03	6.43E-04	7.33E-04	6.49E-04	1.16E-02	1.17E-02	1.69E-03	3.14E-03	9.65E-04	3.96E-03	8.05E-04	4.58E-04	2.63E-02	1.71E-02
Salt Waste	3.70E-03	3.18E-03	3.17E-03	3.95E-03	1.57E-01	3.16E-02	2.87E-02	6.08E-03	3.94E-03	8.77E-02	3.15E-03	3.14E-03	1.67E-02	5.97E-03
Solidified Inorganics	6.76E-02	1.13E-01	1.18E-01	1.16E-01	3.24E+00	4.53E-01	3.86E-01	5.79E-01	2.71E-01	1.08E+00	8.34E-02	2.49E-01	9.96E-01	9.55E-01
Solidified Organics	2.65E+00	2.55E+00	1.46E+00	1.63E+00	1.59E+01	9.09E+00	1.00E+01	2.97E+00	1.85E+00	1.05E+01	1.85E+00	1.35E+00	2.22E+00	2.42E+00
Uncategorized Metal	5.86E-02	5.07E-02	1.61E-01	5.46E-02	1.21E+00	5.75E-01	1.15E+00	1.57E-01	5.29E-01	5.62E-01	1.72E-01	5.69E-02	8.40E-01	8.22E-02
Unknown														

Results

In the 1995 assessment, three VOCs dominated the total VOC source term. Those VOCs were 1,1,1-trichloroethane, carbon tetrachloride, and methylene chloride. Three of the 12 FWFs were the principal contributors to VOC levels in the source term. These FWFs (in order of contribution to the weighted average) were combustibles, solidified organics, and solidified inorganics.

When the screening factors were applied to the 930-drum set used in the 1995 analysis, the total number of drums in the analysis decreased to 800. The resultant weighted average for carbon tetrachloride was reduced from 386 ppmv to 253 ppmv. The dominant FWFs (with respect to net VOC concentration) for VOCs were reduced to two: combustibles and solidified organics. Methylene chloride has been reduced to a very low level because drums with high levels of methylene chloride fail TRAMPAC Rev. 19 and have been eliminated from the analysis.

Results of the 2003 analysis on all available headspace gas data clearly show that the dominant VOCs are 1,1,1-trichloroethane and carbon tetrachloride, and that their weighted averages have decreased from one-third to one-half of the 1995 values. All VOCs were reduced to at least one-half of their 1995 weighted average values in the 2003 analysis. The new methylene chloride weighted average is only two percent of the 1995 value.

Principal contributor in this assessment of VOCs to the weighted average value is the solidified organics FWF, which contributes approximately 92 to 97 percent of the total weighted average of the two major VOCs. A comparison of the weighted source term from the 1995 and 2003 data for 1,1,1-trichloroethane and carbon tetrachloride is shown in Figures 5 and 6.

Fig. 5 Comparison 1,1,1-TCA 1995 & 2003 Data by FWF (PPMV)

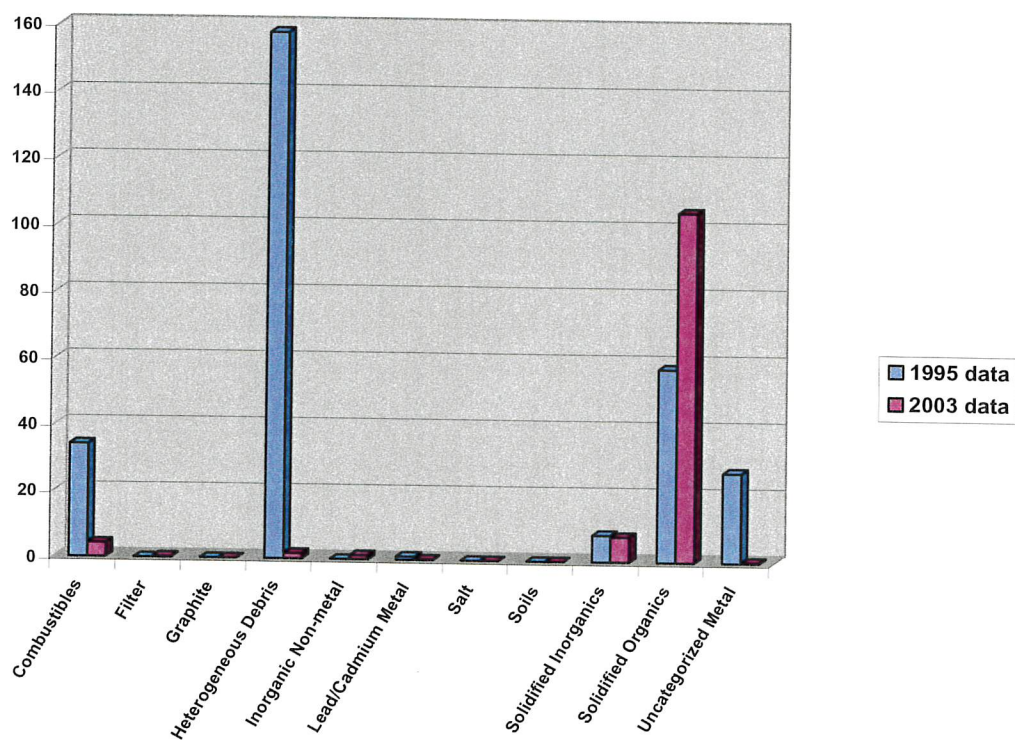
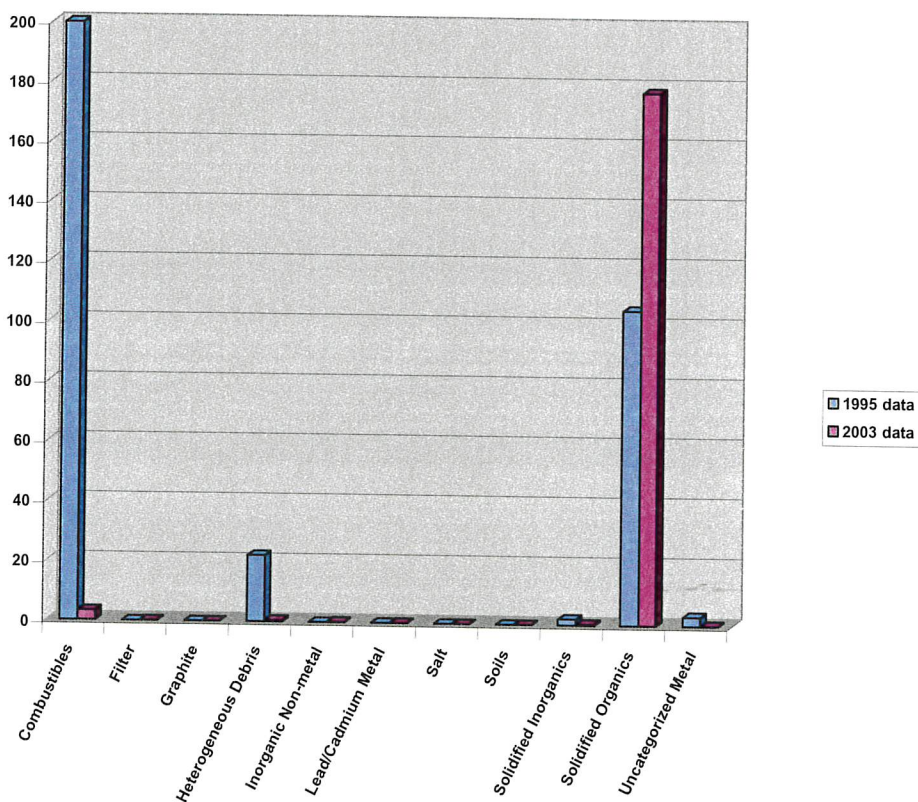


Fig. 6 Comparison Carbon Tetrachloride 1995 & 2003 Data by FWF



Conclusion

Using updated data and a much larger population of headspace gas samplings, a new weighted-average VOC source term for 28 VOCs has been determined. The principal VOCs that contribute to the new source term have been reduced from three in the 1995 data to two in the new data set. These are 1,1,1-trichloroethane and carbon tetrachloride. The FWFs that are principal contributors to the VOC source term have been reduced from three in the 1995 data to one in the new data set. This FWF is solidified organics. The weighted average source term for the two principal VOC contributors in the 2003 data set, 1,1,1-trichloroethane and carbon tetrachloride, decreased to 38 percent and 41 percent, respectively, from their 1995 values.

A breakdown by site for the principal FWF VOC contributor, solidified organics, has been completed and the 2003 Inventory Update (2) indicates that only four sites contain the bulk of the problem. The large sites are RFETS, INEEL, LANL and Hanford, with ETEC and LLNL having a total of an estimated 13 m³.

According to the Inventory Update, all the solidified organic FWF at INEEL originated at RFETS, primarily as VOC-contaminated solidified oils. Thus, all solidified organics headspace gas data in this survey effectively were obtained from RFETS waste and only represent FWF VOC levels for that facility. It is known from process knowledge that this particular RFETS waste stream is highly contaminated with VOCs. The practice at RFETS was to combine waste solvents with waste oil prior to solidification.

The only other DOE facility with a similar process is LANL and, there, the practice was to minimize solvent use through several measures including recycling. Currently, no headspace gas data are available for stored solidified organics for LANL, but process knowledge indicates that the VOC levels should be significantly less than the RFETS solidified organic FWF. The currently stored solidified organics at Hanford are only a few cubic meters and also do not appear to have high VOC levels. The Inventory Update estimates approximately 2,000 m³ of solidified organics, both stored and projected, in the DOE Complex. Of that 2,000 m³, only 1,300 m³ has actually been generated and is currently stored at the sites. RFETS and INEEL represent less than one-third of the 2,000 m³ total amount, but these two sites have approximately one-half the stored volume of solidified organics.

RFETS and INEEL should not be generating any additional solidified organics, thus the volume of problem VOC waste is likely already fixed. It is also reasonable to presume that other sites will manage newly generated solidified organic waste to minimize VOC levels. Because this assessment assumed that all solidified organic FWF for the DOE Complex has average VOC levels which are only representative of RFETS, consequently, the VOC source term for WIPP has been overestimated.

Additionally -- of the 655 m³ solidified organics indicated at INEEL and RFETS -- at least 29 m³ are ion exchange resins or packaging materials and should contain no VOCs. The current assessment indicates the worst case is that only one percent of the total anticipated WIPP volume presently represented by the solidified organics FWF may contain any VOC at average levels greater than 1,000 ppmv in the headspace. Further analysis will likely confirm that LANL and Hanford waste does not contain significant levels of VOCs and the VOC source terms for the solidified organics FWF would be reduced further. In either case, no likely scenario exists that could result in a violation of either the VOC room-based or emission limits for WIPP.

Even conservative acceptance of current data as representative of all solidified organic FWFs for the DOE Complex creates no threat of exceeding WIPP emission standards. This conclusion can be made apart from any further headspace gas sampling. The anticipated volume of solidified FWFs is not sufficiently large to result in a threat to either room-based limits or WIPP emission limits for an open room. Concerns regarding a closed underground room at WIPP require more analysis of scenarios (e.g., a roof fall). However, since WIPP is unlikely to place all high-level VOC-content drums in a single room, there is predictably no threat to WIPP emission standards, even from closed rooms in the repository.

RESOURCES

1. APPENDIX C2, Data Accumulated from Headspace-Gas Analysis, WIPP RCRA Part B Permit Application, DOE/WIPP 91-005, Revision 5
2. LA-UR-03-3427 "Transuranic Waste Inventory Update Report, 2003," June, 2003
3. WIPP Waste Information System data resources provided by Steve Offner, WTS, May 20, 2003
4. "Parameters for Testing Impacts of VOCs as Poisons on Hydrogen Getter Performance", IT Corporation generated for Westinghouse TRU Solutions, May, 2001
5. IDC 003 Organic Setups Study, INEEL, 2001, private communication, M. J. Connolly
6. DOE/CAO-95-1121 "Transuranic Waste Baseline Inventory Report," Revision 3, June, 1996
7. TRAMPAC/Rev.19b "TRUPAC-II Authorization Methods for Payload Control, TRAMPAC, March, 2003
8. Attachment 1, "Examination of Roof Collapse Scenario," WIPP RCRA Part B Permit Application, DOE/WIPP 91-005, Revision 6
9. Appendix D9 "Exposure Assessment for Protection of the Atmosphere," WIPP RCRA Part B Permit Application, DOE/WIPP 91-005, Revision 6

**Statistical Analysis of Volatile Organic Compound Levels
in Transuranic Waste**

Jeffrey C. Myers
Washington Regulatory and Environmental Services
August 22, 2003

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Executive Summary

A Washington Regulatory and Environmental Services (WRES) statistical analysis of volatile organic compounds (VOCs) in the existing Waste Isolation Pilot Plant (WIPP) underground inventory has revealed several important findings. These findings provide the opportunity to modify current methods and procedures so that significant cost savings may be realized without compromising worker safety or risking human health. The two most significant findings are:

- Acceptable knowledge (AK) combined with existing data will supply conservative and protective estimates of the total future VOC load on the WIPP repository.
- Headspace gas sampling and analysis (HSGSA) places an enormous financial burden on the U.S. Department of Energy complex, yet, any value derived appears to be completely absent.

Operating experience to date combined with knowledge of the existing inventory offers the chance to eliminate unnecessary costs for headspace gas sampling. This report details the methods used to evaluate the data and the information on which these findings are based.

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Statistical Analysis of Volatile Organic Compound Levels in Transuranic Waste

Jeffrey C. Myers

Washington Regulatory and Environmental Services (WRES)

I. Introduction

Since the first waste shipment was received in March 1999, the Waste Isolation Pilot Plant (WIPP) has accepted more than 40,000 containers of transuranic (TRU) waste for disposal in the underground repository. Each container placed in the repository has been sampled for volatile organic compounds (VOCs) in the headspace gas (HSG) of the container. These HSG data reside in the WIPP Waste Information System (WWIS) database.

WRES performed a statistical analysis of the current inventory of VOCs in TRU waste in the WIPP repository as compared to the predicted VOC source term. The predicted VOC source term was calculated in 1995 using 930 drums from Idaho National Engineering and Environmental Laboratory (INEEL) and Rocky Flats Environmental Technology Site (RFETS) and was used in support of the WIPP Resource Conservation and Recovery Act (RCRA) Part B Permit application. WRES analysis indicates that actual VOC concentrations in HSG are far below those predicted using the 930-drum data set presented in the WIPP Part B Permit Application. The 930-drum data set was used as a representative population in evaluating complex-wide VOC concentrations in each final waste form (FWF).

The results point strongly to the conclusion that the considerable expenses of HSG sampling are not technically justified. Sufficient data are available to predict average and maximum concentrations in HSG based on acceptable knowledge (AK). Combined with enhanced monitoring of underground VOC concentrations in the ambient air, the HSG data provide a unique opportunity to reap cost savings while simultaneously improving worker health and safety. Details of the WRES data analysis are summarized below.

II. Database

There are two datasets that are compared in this study. The first is the original 930 container set that was used in the WIPP RCRA Permit Application. The second dataset was developed in order to capture HSGSA data generated since the original dataset was reported. This dataset included the following:

- Over 40,000 containers from a query of the WWIS database of VOC concentrations for each measured constituent in drums that have been placed in the WIPP repository from March 1999 to May 2003.
- 2,366 drums from an IT Corporation study on hydrogen getters
- 103 drums of IDC 003 RFETS waste at INEEL analyzed for hydrogen and flammable content impacts on shipping

- The original 930 drum set

Data sets were screened as reported in McCulla and Van Soest (2003). This latter dataset is referred to as the "WIPP Plus" dataset in this paper. A total of 28 VOC compounds were tracked.

This report analyzes data from the solidified organics FWF. It is important to note that no solidified organics wastes have been emplaced at the WIPP to date, nor do such data reside in the WWIS database. The solidified organics data analyzed came from the screened 930-drum data set, the IT Corporation hydrogen getters data set, and the IDC 003 data set.

The WRES statistical analysis was consistent with the analysis performed using the 930-drum data set for the 1995 Part B Permit Application. Both studies recognized the existence of a strongly bimodal data set, i.e. a data set with two different peaks. These peaks generally correspond to the two types of analytical results obtained from headspace gas measurements. The first category represents analyses where a given VOC is not detected or exhibited a very low concentration. This was the case for the majority of the data. The second category represents relatively high concentrations of a particular VOC.

Because of the issue of bimodality, it is inappropriate to apply traditional statistical techniques, which demand that data follow a normal distribution (bell-shaped curve). Hence, both this study and the 930-drum study did not perform uncertainty analyses, calculate upper confidence limits, or examine data sufficiency.

III. VOC Prevalence and Totals

The WRES study addressed 28 individual VOCs currently monitored via HSG sampling at the generator sites. Table 1, *WIPP VOC Mass Inventory*, displays these VOC compounds broken down by FWF categories. The data in Table 1 are WIPP Plus data and represent the sum of the parts per million (ppm) of each of the VOCs per FWF. Thus, the data provide a measure of the mass of each VOC compound placed in or expected to be placed in the repository, detailed by FWF and by VOC constituent. The table can be used to determine which VOCs are most prevalent in a particular FWF, which VOCs are most prevalent in all FWFs, or which FWF contains the greatest prevalence of VOCs.

Table 1 benefits the analysis by providing a method to group and evaluate any particular compound. Table 1 winnows the VOCs into two relatively distinct groups: (1) Those which distinguish themselves as major contributors to the total VOC load on the WIPP repository; and, (2) Those which are minor or negligible contributors to the total mass load. In addition, the major and minor contributors to each FWF can also be gleaned from Table 1.

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Focusing first on the FWFs, Table 1 (WIPP VOC Mass Inventory) shows that the solidified organics stream contains by far the largest amount (mass) of the VOCs (68 percent). The solidified organics FWF dwarfs the remaining FWFs in terms of contribution by mass. The next largest FWF is combustibles, composing approximately 16 percent of the total mass. The remaining 14 percent of the mass is divided amongst the nine other FWFs, with the largest of these remaining FWFs composing a mere six percent of the total, or on average about one and one-half percent of the total VOC load.

Looking next at the impact of the 28 individual VOC compounds on the repository as a whole, carbon tetrachloride emerges as the largest contributor, comprising approximately 28 percent of the total mass when totaled across all 11 FWFs. Carbon tetrachloride is followed in abundance by 1,1,1-trichloroethane at 19 percent. These two compounds contribute nearly half of the VOC mass (approximately 47 percent). The 26 remaining compounds contribute less than nine percent each, with the majority of them (approximately 60 percent) contributing less than one percent of the total VOC load.

Table 1 can be converted easily from a total mass perspective to a concentration per drum standpoint. Table 2, *Average VOC Concentrations by Analyte and FWF*, lists the same VOCs and the same FWFs as in Table 1, but Table 2 provides the average concentration of a VOC in each of the FWFs. As in Table 1, the far right column summarizes the average VOC concentration across all FWFs. Table 3, *Prevalence of VOCs by Mass in WIPP Plus Inventory*, is a subset of Table 1 that lists the 28 VOCs in order of decreasing prevalence and totaled across all 11 FWFs. As described above, the first three compounds comprise over half of the inventory, with percentages quickly dropping to below one percent in total contribution. As with Table 1, Table 3 allows the significant versus less significant VOC contributors to be winnowed out and ranked quickly.

VOC (Total ppm)	Final Waste Form										
	Combustible	Filter	Graphite	Heterogeneous	Inorganic Non-Metal	Lead / Cadmium	Salt	Solidified Organics	Solidified Inorganics	Uncategorized Metal	Soils
CIS-1,2-DICHLOROETHYLENE	13,324	703	1,806	9,197	704	246	752	45,380	5,944	1,146	NA
1,1,1-TRICHLOROETHANE	426,431	2,858	3,308	8,649	2,497	8,998	763	1,710,376	58,884	9,850	NA
1,1,2,2-TETRACHLOROETHANE	12,886	485	1,111	8,910	688	290	753	45,359	4,859	1,192	NA
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	66,539	15,730	1,135	8,286	660	540	804	564,987	57,233	1,352	NA
1,1-DICHLOROETHANE	13,510	1,242	1,363	8,578	1,068	439	1,374	63,968	9,761	1,251	NA
1,1-DICHLOROETHYLENE	15,758	996	1,461	7,227	886	389	830	50,853	15,390	1,266	NA
1,2,4-TRIMETHYLBENZENE	9,072	541	1,021	7,714	702	292	725	48,534	5,165	1,246	NA
1,2-DICHLOROETHANE	12,796	824	1,178	7,574	784	251	774	46,432	5,873	1,227	NA
1,3,5-TRIMETHYLBENZENE	8,270	513	900	1,607	668	238	713	42,006	4,952	1,230	NA
ACETONE	130,251	37,423	21,750	64,709	15,409	7,963	9,495	441,024	49,957	42,030	NA
BENZENE	15,013	1,936	1,264	9,009	1,057	335	222	47,398	9,937	5,143	NA
BROMOFORM	12,245	579	994	6,816	599	216	742	44,146	5,171	1,284	NA
CARBON TETRACHLORIDE	286,686	3,983	1,312	8,598	3,326	8,147	791	2,967,688	22,736	4,649	NA
CHLOROFORM	14,169	623	891	9,320	667	250	720	47,772	4,937	1,185	NA
CHLOROBENZENE	32,308	2,223	1,258	8,509	1,640	647	250	60,860	5,468	1,519	NA
CYCLOHEXANE	24,760	876	1,123	1,664	1,618	277	767	65,703	6,971	1,123	NA
ETHYL BENZENE	17,550	806	1,151	8,760	749	323	770	45,968	8,872	1,744	NA
ETHYL ETHER	14,585	1,018	1,500	9,452	1,193	362	2,138	54,674	8,763	1,363	NA
METHANOL	229,524	49,498	26,258	59,758	22,720	6,132	4,808	506,892	168,582	26,673	NA
METHYLETHYL KETONE	75,976	9,073	10,925	46,680	5,250	1,936	8,294	287,853	36,604	11,752	NA
METHYL ISOBUTYL KETONE	103,620	3,511	10,414	51,595	4,590	898	7,071	315,205	33,020	17,473	NA
METHYLENE CHLORIDE	154,913	3,042	1,588	39,660	1,871	833	1,312	81,212	16,498	6,093	NA
m-XYLENE	31,735	1,050	1,805	11,750	997	369	1,404	53,130	18,845	3,250	NA
n-BUTYL ALCOHOL	142,466	6,123	13,480	49,891	10,116	1,639	24,805	288,688	55,305	15,723	NA
o-XYLENE	21,313	670	1,046	9,315	795	291	751	59,451	7,170	2,428	NA
TETRACHLOROETHYLENE	12,859	691	943	8,717	637	214	735	44,866	8,556	1,325	NA
TOLUENE	38,940	7,820	802	11,259	4,785	1,544	388	56,772	36,154	7,802	NA
TRICHLOROETHYLENE	13,278	1,986	1,189	7,112	2,510	1,420	1,326	60,884	13,847	1,322	NA
TOTAL	1,952,777	156,823	112,976	484,296	89,186	45,479	74,277	8,149,882	685,454	173,641	NA
Note: All values assume an equal amount of headspace gas in each container											

Table 1: WIPP VOC Mass Inventory (WIPP Plus Data)

VOC (Average ppm per Drum)		Final Waste Form											
Combustible	Filter	Graphite	Heterogeneous	Inorganic Non-Metal	Lead / Cadmium	Salt	Solidified Organics	Solidified Inorganics	Uncategorized Metal	Soils	Total	Average for All FWFs	
(cis)-1,2-DICHLOROETHYLENE	2.31	0.35	0.46	2.14	0.37	0.51	0.35	247	0.43	0.71	255	1.74	
1,1,1-TRICHLOROETHANE	87.8	1.92	1.77	2.36	2.36	81.1	0.36	9,098	7.05	6.40	9,289	49.1	
1,1,2,2-TETRACHLOROETHANE	2.24	0.27	0.47	2.08	0.37	0.61	0.35	216	0.38	0.73	224	1.7	
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	11.6	7.99	0.60	1.93	0.35	1.13	0.38	2,743	4.58	0.84	2,772	15.8	
1,1-DICHLOROETHANE	2.35	0.62	0.58	2.00	0.57	0.92	0.65	317	0.71	0.77	326	2.3	
1,1-DICHLOROETHYLENE	2.73	0.50	0.62	1.69	0.47	0.81	0.39	253	1.13	0.78	262	2.1	
1,2,4-TRIMETHYLBENZENE	2.03	0.30	0.44	1.41	0.38	0.63	0.34	232	0.40	0.83	239	1.5	
1,2-DICHLOROETHANE	2.22	0.41	0.50	1.77	0.41	0.52	0.36	221	0.43	0.76	228	1.7	
1,3,5-TRIMETHYLBENZENE	1.84	0.26	0.38	1.32	0.36	0.51	0.34	201	0.37	0.81	207	1.3	
ACETONE	22.7	18.9	11.5	15.1	10.1	16.7	4.46	2,100	4.39	25.9	2,230	18.0	
BENZENE	2.61	0.99	0.67	2.12	0.56	0.70	1.21	239	0.88	3.22	252	2.0	
BROMOFORM	2.12	0.29	0.42	1.59	0.32	0.45	0.35	210	0.38	0.79	217	1.6	
CARBON TETRACHLORIDE	51.1	2.07	0.58	2.01	1.79	18.1	0.37	14,132	1.66	2.90	14,213	72.8	
CHLOROETHYLENE	2.46	0.31	0.38	2.17	0.35	0.52	0.34	228	0.36	0.73	236	1.8	
CHLOROFORM	5.83	1.12	0.66	2.00	0.88	1.38	0.83	290	0.40	0.94	304	2.5	
CYCLOHEXANE	5.55	0.44	0.48	1.37	0.98	0.58	0.36	316	0.51	0.74	327	2.3	
ETHYL BENZENE	3.05	0.40	0.49	2.04	0.40	0.67	0.36	219	0.65	1.08	228	1.9	
ETHYL ETHER	2.53	0.51	0.64	2.20	0.63	0.75	1.01	259	0.64	0.84	269	2.1	
METHANOL	40.4	25.0	13.9	14.0	15.0	12.7	16.0	2,419	15.9	16.4	2,588	24.2	
METHYL ETHYL KETONE	13.2	4.55	4.63	10.9	3.44	4.02	3.90	1,371	2.66	7.24	1,426	10.9	
METHYL ISOBUTYL KETONE	18.0	1.76	4.41	12.0	2.41	1.86	3.33	1,501	2.40	10.8	1,558	12.0	
METHYLENE CHLORIDE	27.3	1.60	0.84	9.37	1.02	1.76	0.65	392	1.28	3.82	440	6.7	
m-XYLENE	5.56	0.53	0.77	2.79	0.64	0.77	0.66	253	1.38	2.08	268	2.7	
n-BUTYL ALCOHOL	24.9	3.19	5.98	11.7	5.34	3.41	11.70	1,375	4.27	9.69	1,455	13.4	
p-XYLENE	3.70	0.34	0.44	2.17	0.42	0.60	0.35	283	0.52	1.51	293	2.3	
TETRACHLOROETHYLENE	2.23	0.35	0.40	2.03	0.34	0.44	0.35	216	0.63	0.82	224	1.7	
TOLUENE	7.27	4.95	0.54	2.87	3.60	6.13	2.18	309	3.65	5.67	346	3.7	
TRICHLOROETHYLENE	2.40	1.02	0.50	1.67	1.40	3.70	0.63	304	1.14	0.83	317	2.3	
TOTAL	358	81	54	117	55	162	53	39,944	59	109	40,991	NA	

Table 2: Average VOC Concentrations by Analyte and FWF (WIPP Plus Data)

PREVALENCE OF VOCs IN FWFs BY MASS IN CURRENT WIPP INVENTORY: WIPP Plus, June 2003		
VOC	% of Total ppm	Rank
CARBON TETRACHLORIDE	27.8	1
1,1,1-TRICHLOROETHANE	18.7	2
METHANOL	9.2	3
ACETONE	6.9	4
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	6.0	5
n-BUTYL ALCOHOL	5.1	6
METHYL ISOBUTYL KETONE	4.6	7
METHYL ETHYL KETONE	4.1	8
METHYLENE CHLORIDE	2.6	9
TOLUENE	1.4	10
m-XYLENE	1.04	11
CHLOROFORM	0.96	12
CYCLOHEXANE	0.88	13
TRICHLOROETHYLENE	0.88	14
p-XYLENE	0.87	15
1,1-DICHLOROETHANE	0.86	16
ETHYL ETHER	0.80	17
1,1-DICHLOROETHYLENE	0.80	18
BENZENE	0.77	19
ETHYL BENZENE	0.73	20
CHLOROBENZENE	0.68	21
TETRACHLOROETHYLENE	0.67	22
(cis)-1,2-DICHLOROETHYLENE	0.66	23
1,2-DICHLOROETHANE	0.65	24
1,1,2,2-TETRACHLOROETHANE	0.64	25
BROMOFORM	0.61	26
1,2,4-TRIMETHYLBENZENE	0.58	27
1,3,5-TRIMETHYLBENZENE	0.51	28
based on ppm sum		
Note: All values assume an equal amount of headspace gas in each container		

Table 3: Prevalence of VOCs By Mass in WIPP Plus Inventory

Taking a slightly different perspective -- a by-waste form approach -- Table 4, *Prevalence of VOCs in FWFs by Mass*, uses the information in the WIPP Plus dataset, which includes solidified organics, to order the 11 FWFs by increasing VOC contribution to the total WIPP VOC inventory. Table 4 shows that solidified organics comprise a majority of the VOCs at approximately 68 percent of the mass. The next largest FWF contributor is the combustible waste stream, which accounts for a little over 16 percent of the mass. The remaining nine FWFs contribute only about 15 percent of the total VOC source term.

PREVALENCE OF VOCs IN FWFs BY MASS IN CURRENT WIPP INVENTORY: WIPP Plus, June 2003		
FWF	% of Total ppm	Rank
Solidified Organics	68.3%	1
Combustible	16.4%	2
Solidified Inorganics	5.7%	3
Heterogeneous	4.1%	4
Uncategorized Metal	1.5%	5
Filter	1.3%	6
Graphite	0.9%	7
Inorganic Non-Metal	0.7%	8
Salt	0.6%	9
Lead / Cadmium	0.4%	10
Soils	0.00%	11
Total	100.0%	

Table 4: Prevalence of VOCs in FWFs by Mass

Table 5, *Relative Size of Waste Streams by Volume*, shows the ranking of the relative sizes of the waste streams (volumes) in terms of the number of containers emplaced at WIPP. Almost 40 percent of the volume of waste emplaced to date is composed of FWF solidified inorganic materials. The solidified inorganics FWF is followed by the salt, combustible and heterogeneous waste streams. These four FWFs contribute more than 78 percent of containers accepted by the repository to date, with the remaining seven FWFs contributing a mere 22 percent of the volume of waste.

Relative Size of Waste Streams By Volume	
Final Waste Form (FWF)	% of Total
Solidified Inorganics	39.8%
Salt	14.7%
Combustible	13.5%
Heterogeneous	10.1%
Inorganic Non-Metal	6.4%
Graphite	6.0%
Filter	4.4%
Uncategorized Metal	3.6%
Lead/Cadmium	1.1%
Solidified Organics*	0.5%
Soils	0.0%
*not yet emplaced in the WIPP	

Table 5: Relative Size of Waste Streams by Volume

Table 4 indicates clearly that the largest percentage of VOCs is coming from the projected solidified organics waste stream, whereas Table 5 shows that the solidified organics waste stream comprises only approximately one-half of one percent of the total volume entering WIPP. Conversely, solidified inorganics contribute almost 40 percent of the total volume coming into WIPP, yet only account for about six percent of the total VOCs. By contrast, the combustible waste stream contributes sizable volumes as well as mass to the WIPP inventory. Section V will discuss a method for assessing the joint contribution to the repository load made by simultaneously evaluating the mass load along with the size of the waste stream.

IV. Comparison of WIPP Plus Data to Predictions Using 930 Drums

The WIPP Plus data provide a representation of what has already been sent to WIPP and what can be reasonably expected to continue to enter the repository. The risk evaluation regarding VOCs stored at WIPP was based on the VOC load predicted using the 930-drum data set. WRES statistical analysis has determined that the VOC load on WIPP has likely been significantly overestimated. This conclusion is based on the fact that the first 45,000 drums disposed (approximately) contain far less VOC load than would have been predicted using the 930-drum data set. This overestimation has a benefit, however. Using the 930-drum data set as a predictor, experience to date shows that the future VOC mass will likely be overestimated consistently. Overestimation provides a conservative assessment of the future VOC load and, therefore, the associated risks. Details supporting this conclusion appear below.

Table 6, *Comparison of Actual Waste Data (WIPP Plus) to Predicted*, summarizes the expected versus actual percentages of each VOC for the WIPP Plus and 930-drum data sets. Notable exceptions occur with methylene chloride and carbon tetrachloride.

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Because of the use of chemical synonyms, not all analytes could be correlated between datasets as indicated by the "NA" in the Table.

VOC (Total ppm)	FINAL WASTE FORM					
	% of Total VOCs		RANK		VOC Cumulative Sum	
	WIPP Plus	930 DRUMS	WIPP Plus	930 DRUMS	WIPP Plus	930 DRUMS
CARBON TETRACHLORIDE	27.8	21.5	1	1	27.8	21.5
1,1,1-TRICHLOROETHANE	18.7	18.1	2	3	46.5	39.6
METHANOL	9.2	12.2	3	4	55.7	51.8
ACETONE	6.9	4.6	4	5	62.6	56.4
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	6.0	NA	5	NA	68.6	56.4
n-BUTYL ALCOHOL	5.1	NA	6	NA	73.7	56.4
METHYL ISOBUTYL KETONE	4.6	4.5	7	6	78.3	60.9
METHYL ETHYL KETONE	4.1	3.6	8	7	82.4	64.5
METHYLENE CHLORIDE	2.6	21.0	9	2	85.0	85.6
TOLUENE	1.4	1.11	10	11	86.4	86.7
m-XYLENE	1.04	1.10	11	12	87.5	87.8
CHLOROFORM	0.96	1.45	12	9	88.4	89.2
CYCLOHEXANE	0.88	NA	13	NA	89.3	89.2
TRICHLOROETHYLENE	0.88	1.43	14	10	90.2	90.7
o-XYLENE	0.87	0.91	15	13	91.1	91.6
1,1-DICHLOROETHANE	0.86	0.58	16	18	91.9	92.1
ETHYL ETHER	0.80	0.76	17	14	92.7	92.9
1,1-DICHLOROETHYLENE	0.80	0.66	18	17	93.5	93.6
BENZENE	0.77	0.53	19	22	94.3	94.1
ETHYL BENZENE	0.73	0.66	20	16	95.0	94.8
CHLOROBENZENE	0.68	0.71	21	15	95.7	95.5
TETRACHLOROETHYLENE	0.67	0.54	22	19	96.3	96.0
(cis)-1,2-DICHLOROETHYLENE	0.66	0.51	23	24	97.0	96.5
1,2-DICHLOROETHANE	0.65	0.52	24	23	97.7	97.0
1,1,2,2-TETRACHLOROETHANE	0.64	0.53	25	21	98.3	97.6
BROMOFORM	0.61	0.54	26	20	98.9	98.1
1,2,4-TRIMETHYLBENZENE	0.58	NA	27	NA	99.5	98.1
1,3,5-TRIMETHYLBENZENE	0.51	NA	28	NA	100.0	98.1
TOTAL	100.00					

Note: All values assume an equal amount of headspace gas in each container

Table 6: Comparison of Actual Waste Data (WIPP Plus) to Predicted

Figure 1, *Scatter Plot and Regression on 930-Drum Data vs. WIPP Plus Data*, shows a scatter plot and regression line for the WIPP Plus versus 930-drum data. The x-axis plots the percentage of the total mass of VOCs represented by the VOCs in a particular FWF based on the 930-drum data set. The y-axis plots the percentage of the total mass of VOCs represented by a FWF in the WIPP Plus data to date. The red line indicates the fitted linear regression model that can be used as a predictor. In other words, using the percentage of total VOCs in the 930-drum data set for a particular FWF, one can derive an estimate of how much mass of the VOC has actually been accepted into WIPP or how much is expected to be accepted in the future. The blue lines represent 95 percent prediction intervals around the regression line.

The graph confirms the results presented in Table 6 (i.e., there is a good correlation between predicted versus actual.) Regression analysis produced a correlation coefficient of 0.81, with an r^2 value of 0.65. The r value is a unitless measure of the degree of association between the two variables. An r value of zero indicates no association; an r value of 1 indicates perfect association. These values confirm that using the 930-drum data set is a conservative way to predict future VOC loads on the repository.

WIPP VOC Inventory

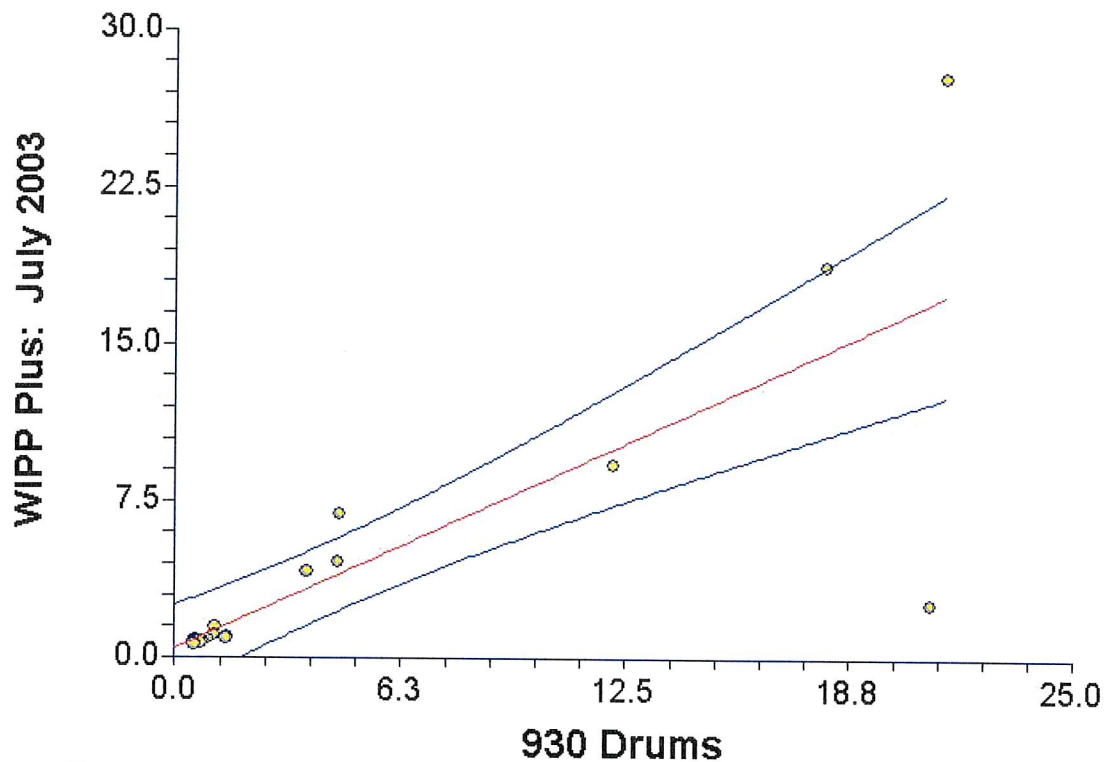
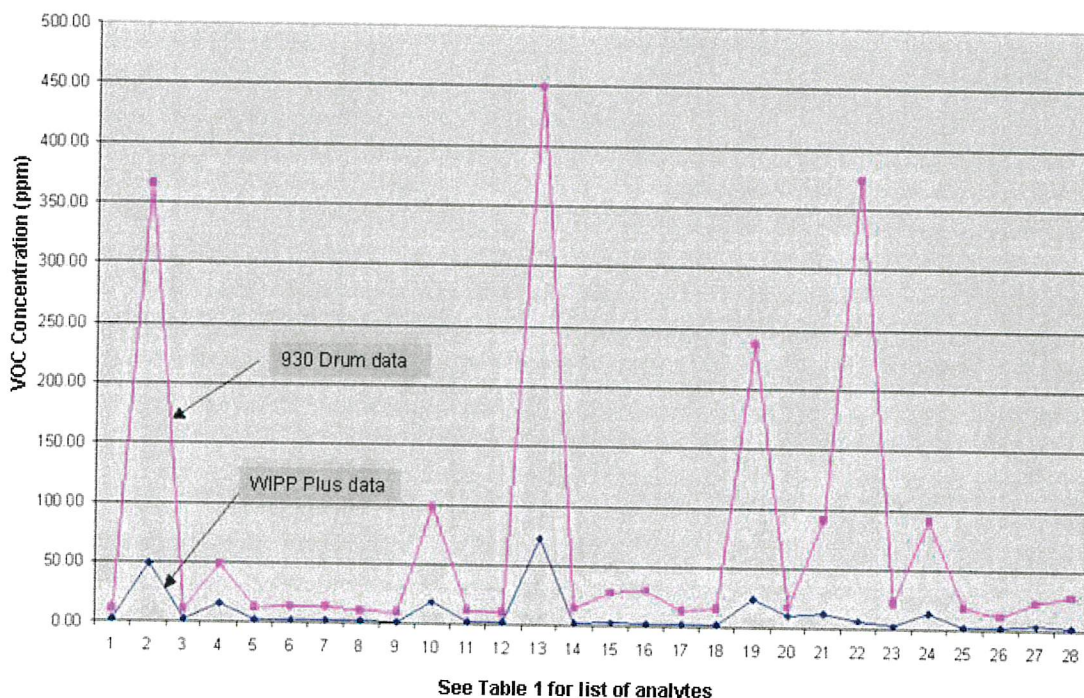


Figure 1: Scatter Plot and Regression on 930-Drum Data vs. WIPP Plus Data

Figure 2, *Comparison of Average VOC Concentrations: 930-Drum vs. WIPP Plus Data*, is a graph illustrating the comparison of VOC concentrations estimated during the 930-drum study versus the actual VOC data from HSG measurements that accompany drums placed in the WIPP repository. The 28 VOCs are plotted along the *x*-axis and the VOC concentrations in parts per million are plotted on the *y*-axis. The graph shows that the VOC concentration estimate from the 930-drum study is -- without exception -- higher than the actual VOC concentrations admitted to WIPP for each of the 28 VOCs.

In most cases, the 930-drum study estimate is, at a minimum, several times (two to nine times) the real HSG data in drums placed to date. Note that, in a number of cases, the overestimation incurred by the 930-drum study is more than an order of magnitude above the true value. Again, these results indicate that estimating the VOC load on the repository with the 930-drum study is highly conservative. Now that over 45,000 actual data are available from HSG sampling, the conclusion of the 930-drum study provides an approximate upper bound expected on drum VOC concentrations. Whereas, in 1995, the 930-drum data set was considered to be representative, actual data from operating, experience now indicates that the 930-drum data set predictions categorically overestimate the actual VOC source term.

WIPP Plus vs. 930 drums

**Figure 2****Comparison of Average VOC Concentrations: 930-Drum vs. WIPP Plus Data**

Considering Figures 1 and 2, collectively, the nature and masses of the waste can be predicted with sufficient accuracy to ensure worker safety and long-term protection of human health. Figure 1 and Table 6 indicate that predicted versus actual values show close correlation in most cases, providing a level of assurance that future wastes will do the same. More importantly, however, Figure 2 shows that using 930-drum data to predict VOC load on WIPP will categorically overestimate the mass.

The overestimation can be viewed in terms of a “safety factor” that provides a level of confidence that the total source term on WIPP will not exceed what was estimated. Safety factors, calculated by dividing the estimated average concentration per drum in the 930-drum data set by the actual average concentration per drum, fall between approximately two and 12 for most VOCs. The notable exception is methylene chloride, with a safety factor of 54.5.

Based on data associated with drums received at WIPP to date, every one of the 28 analyzed VOC masses has been overestimated and has a safety factor greater than 1.0. Safety factors greater than one indicate overestimation and a level of conservatism, compared to safety factors that are less than one, which indicate underestimation and a

potential risk to worker safety and human health. Therefore, prediction using the 930-drum data set is expected to produce a conservative estimate.

V. Analysis of Prevalence of a VOC vs. Volume of an FWF

Previous tables have shown that certain VOCs are strongly prevalent in WIPP inventory. Similarly, certain FWFs contain overwhelming amounts of the mass of VOCs. One question that arises is whether one can determine the sensitivity between volume and mass contributions of the various waste streams when volume and mass are considered jointly. For instance, the solidified organics FWF contributes about 68 percent of the mass of VOCs (rank #1) that may be eligible for disposal in the repository, but only accounts for about one-half of one percent of the total inventory by volume (rank #10) i.e., a very small volume. Conversely, the solidified inorganics FWF contributes about 40 percent of the total waste volume in the repository (rank #1), but only contributes about six percent of the VOC mass (rank #3). Note also the combustible FWF, which ranks high (#2 and #3) in prevalence for both mass and size (volume) respectively.

From a practical perspective, one might ask: “If a waste stream is high in organics but small in size, is this of greater concern than a waste stream that has a lesser VOC mass but more volume?” One approach to answering this question is to take the percentage data in each category (volume and mass) and multiply them. This will create a service variable that provides a relative measure of the “discomfort” associated with a particular FWF.

DISCOMFORT FACTORS						
FINAL WASTE FORM (FWF)	FACTOR		RANK		PERCENTAGE	
	930 Drums	WWIS Plus	930 Drums	WWIS Plus	930 Drums	WWIS Plus
SOLIDIFIED INORGANICS	1.1	1.9	1	1	13%	37%
COMBUSTIBLE	5.8	1.8	2	2	65%	35%
HETEROGENEOUS	0.91	0.86	3	3	10%	16%
UNCATEGORIZED METAL	0.25	0.10	4	4	3%	2%
SALT	0.0006	0.073	10	5	0%	1%
FILTER	0.020	0.054	6	6	0%	1%
GRAPHITE	0.0038	0.045	8	7	0%	1%
INORGANIC NON-METAL	0.0075	0.038	7	8	0%	1%
SOLIDIFIED ORGANICS	0.820	0.273	5	9	9%	5%
LEAD/CADMIUM	0.0008	0.003	9	10	0%	0%
SOILS	0.0000	0.0000	11	11	0%	0%

Note: All values assume an equal amount of headspace gas in each container

Table 7: Discomfort Factors for Selected Data Sets

Table 7, *Discomfort Factors for Selected Data Sets*, displays the results of the discomfort factor calculation from the 930 drum study and the WIPP Plus database. The table indicates that the solidified inorganics and combustible FWFs exhibit a joint concern

level of almost two for the wastes that are already in the repository. Heterogeneous wastes account for just under one percent, with the remaining eight FWFs ranking at 0.1 or less. The solidified organic FWF, while contributing a large percentage of the mass, has a discomfort factor about seven times less than that for solidified inorganics.

VI. Representativeness of the Data

The data analyzed by WRES represented each of the 11 FWFs with the exception of the soil FWF. Table 8, *Number of FWF Waste Streams Emplaced in the WIPP*, contains the number of each type of FWF that was available for the analysis. Table 8 shows that the combustible, heterogeneous, and inorganic non-metal FWFs are well represented by the current WIPP inventory, containing 15 or more example waste streams of each FWF. Solidified inorganic contains nine waste streams, providing a reasonable number of examples. The remaining FWFs, however, contain only zero to three waste streams. Results based on these waste streams are most likely of lesser confidence than those that have a greater representation.

Final Waste Form (FWF)	Number of Waste Streams
Combustible	15
Filter	3
Graphite	5
Heterogeneous	17
Inorganic Non-Metal	10
Lead/Cadmium	3
Salt	3
Soils	0
Solidified Inorganics	9
Solidified Organics	0
Uncategorized Metal	2
Total	67

Table 8
Number of FWF Waste Streams Emplaced at WIPP

VII. VOCs to Monitor in the Underground

Because certain VOC concentrations in the WIPP Plus data differed from the concentrations in the 930-drum data set, WRES reanalyzed the VOC risks to confirm that those compounds currently being monitored in the underground are the appropriate ones. WRES used the methodology employed in Appendix D-13 of the RCRA Part B Permit Application, where VOC concentrations were weighted in conjunction with their respective risk factors to determine which VOCs contributed to 99 percent of the risk.

Table 9 lists the compounds analyzed in Appendix D-13 along with the calculations performed using the WIPP Plus data. Results were fairly similar in the carcinogen category, where six of the seven existing VOCs were determined to contribute to 99 percent of the risk. Methylene chloride was no longer determined to be a contributor. For non-carcinogens, (cis)-1,2-dichloroethylene and methyl ethyl ketone were also determined to contribute to 99 percent of the risk.

Risk Class	VOC	Molecular Weight	Headspace Gas Concentration (ppm)	Headspace Gas Concentration (per m ³)	Unit Risk (m ³ per microgram)	Score	Percent
Carcinogens	Benzene	78.11	2.01	6421	0.00000830	0.05329039	0.42
	Bromoform	252.77	1.60	16539	0.00000110	0.01819308	0.14
	Carbon tetrachloride	153.84	72.8	458003	0.00001500	6.87005178	53.6
	Chloroform	119.39	2.52	12304	0.00002300	0.28298566	2.21
	Methylene chloride	84.94	6.75	23447	0.00000047	0.01102001	0.09
	1,1-Dichloroethylene	96.95	2.09	8286	0.00005000	0.41431648	3.23
	1,2-Dichloroethane	98.96	1.71	6920	0.00002600	0.17992738	1.40
	1,1,2,2-Tetrachloroethane	167.86	1.68	11533	0.00005800	0.66888675	5.22
	Tetrachloroethylene	165.85	1.75	11869	0.00000058	0.00688414	0.05
	1,1,1-Trichloroethane	133.4	49.1	267858	0.00001600	4.28573590	33.4
	1,1,2-Trichloroethane	133.42					
	Trichloroethylene	131.4	2.31	12413	0.00000170	0.02110204	0.16
	Vinyl chloride	62.5					
Non-Carcinogens	Carbon disulfide	76.14					
	Chlorobenzene	112.56	1.77	8.1	0.00000830	0.00006762	13.3
	(cis)-1,2-Dichloroethylene	96.95	1.74	6.9	0.00000830	0.00005726	11.3
	Isobutanol	74.12					
	Methyl ethyl ketone	72.1	10.9	32.1	0.00000830	0.00026675	52.6
	Toluene	92.13	3.70	13.9	0.00000830	0.00011570	22.8
	Trichlorofluoromethane	137.38					

Table 9: Calculation of Risk Contribution

VIII. Conclusions

The following conclusions can be drawn from the analysis of the VOC data from containers disposed in the WIPP repository:

1. Estimated proportions and actual proportions match closely. Relative proportions of the 28 VOCs monitored during HSG sampling exhibit relatively little fluctuation between the 930-drum study and the WIPP Plus database. This indicates that either database may be used as a reasonable predictor of the proportion of a particular VOC will contribute to the total VOC load on WIPP.
2. The total anticipated VOC load on the repository is overestimated. The data prove that average VOC concentrations in the containers that have been accepted into WIPP are less than those predicted by the 930-drum study. This means that use of the 930-drum inventory as a predictor should result in a conservative (excessive) estimate of the amount of VOC mass that can be expected to be in future waste streams.

3. Based on conclusion #2, if the risks posed by VOCs were acceptable based on the 930-drum study, clearly the risks have been reduced and will remain below acceptable levels.
4. Potential problem waste streams can be identified by use of the discomfort factor and special procedures can be developed to manage FWFs of concern if necessary.
5. HSG sampling to date has not contributed to a greater understanding of (1) volumes of VOCs entering WIPP in total; (2) proportions of particular VOCs entering WIPP; or, (3) understanding which waste streams contain the largest amounts of VOCs. Based on this evidence, HSG sampling can be considered an unproductive and unnecessary expense to the DOE complex and should be eliminated. AK has proved sufficient to determine volumes, masses and proportions, and has been confirmed using data from more than 45,000 drums.
6. Given the stability of predicted versus actual proportions and mass of wastes coming to WIPP, relying on AK appears to be an appropriate approach. However, increased air monitoring of VOC concentrations in the ambient air in the repository would provide a practical, efficient, and more cost-effective way to confirm worker health and safety and should replace HSG sampling.

IX. Discussion

The estimates made regarding the proportions and load of VOCs on the WIPP repository made in 1995 represent a good-faith prediction based on what was agreed to be the best and most appropriate information available. Seven years later, we find ourselves in a "that was then, this is now" situation. Waste shipments have been accepted on a regular basis for more than four years and a body of over 45,000 data has been accumulated. This wealth of actual data serves to confirm the reliability of initial estimates.

The initial estimates can be considered reliable because they have overstated the mass load, which contributes positively to ensure worker safety as well as human health and safety. In addition, initial versus actual proportions of individual VOCs remain highly constant, ensuring that risks will not change due to differences in relative proportions of VOCs that would subsequently alter risk estimates.

Even at levels predicted by the 930-drum data set, safe operation of the repository can be easily achieved through proper ventilation and monitoring. Operations to date further demonstrate that a safe environment can be maintained. WIPP has an exemplary record for maintaining underground air quality.

Due to low levels of VOCs actually observed, it is not possible to place waste containers in a configuration where catastrophic events such a roof fall could produce either a short-term risk to workers or a long-term risk to boundary residents. Data produced by

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monitoring the ambient air in the underground to date have shown that VOC levels are far below risk levels, lower explosive limits, or other thresholds of concern.

Starting with a situation where health risks are highly unlikely -- if not unattainable -- provides an enormous margin of comfort and safety for the operation. This comfort factor is completely unavailable in many industrial operations. Coal mining is one example of an industry where problem VOCs in the air create risks. Without proper ventilation (continuous dilution with fresh air), methane gas in an underground coal mine can cause devastating explosions. At WIPP, the possibility for such a scenario is remote to the point of improbability.

WIPP has a proven track record for maintaining safety from VOCs in the underground. In the event that VOC levels in containers should increase in the future, indications are overwhelming that safety could be maintained via operational modifications, such as modification of monitoring and ventilation activities.

To create scenarios that even remotely pose a risk, VOC concentrations in the containers would have to exceed levels allowed by transportation restrictions. Thus, a dramatic conclusion emerges: The possibility of VOCs being a health or safety risk is self-limiting.

Given this situation, the benefit of performing HSG sampling to ensure safety in the underground and to boundary residents disappears. HSG sampling places an enormous financial burden on the DOE complex, yet the value derived appears to be completely absent.

X. References

APPENDIX C2, Data Accumulated from Headspace-Gas Analysis, WIPP RCRA Part B Permit Application, DOE/WIPP 91-005, Revision 5

DOE/CAO-95-1121 "Transuranic Waste Baseline Inventory Report", Revision 3, June, 1996

WIPP Waste Information System data resources provided by Steve Offner, WTS, May 20, 2003

McCulla, William H and Gregory D. Van Soest, (2003) Analysis of Volatile Organic Compound Levels in the Transuranic Waste Inventory, LANL-EES-12

D R A F T

**Technical Evaluation Report
for WIPP Room-Based VOC Monitoring**

**Wesley Boatwright
Washington Regulatory & Environmental Services
Waste Isolation Pilot Plant
Carlsbad, New Mexico**

Executive Summary

This document details the proposed plan to exchange headspace gas sampling with monitoring in the open panel in the Waste Pilot Plant (WIPP) underground. Background information involving volatile organic compound (VOC) emissions is discussed in this report. The information includes discussion of the 1996 permit application, New Mexico Environment Department (NMED) risk scenarios, and current methods that WIPP is using to determine compliance with the room based limits described in the WIPP hazardous waste facility permit (HWFP). This report also discusses new information on VOCs received from current headspace gas sampling results and closed room VOC monitoring. WIPP proposes that by monitoring the open and closed rooms in the active panel compliance with the room-based limits can be demonstrated. The proposed methods of determining compliance described in this document will be conducted in the absence of headspace gas sampling, which is the current method of maintaining compliance with the requirements in the HWFP. Discussion points about this proposed monitoring include methodology and actions to protect worker safety are noted in the technical evaluation report.

Technical Evaluation Report of WIPP Room-Based VOC Monitoring

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Acronym List

ACGIH	American Conference of Governmental Industrial Hygienists
DOE	Department of Energy
EPA	Environmental Protection Agency
ETEC	Energy Technology Engineering Center
FWF	Final Waste Form
HBL	Health Based Level
HSG	Headspace Gas
HWDU	Hazardous Waste Disposal Unit
HWFP	Hazardous Waste Facility Permit
IDLH	Immediately Dangerous to Life and Health
INEEL	Idaho National Environmental Engineering Laboratory
LANL	Los Alamos National Laboratory
MDL	Method Detection Limit
NMED	New Mexico Environment Department
NOD	Notice of Deficiency
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
PMR	Permit Modification Request
Ppbv	Parts Per Billion by Volume
Ppmv	Parts Per Million by Volume
RCRA	Resource Conservation Recovery Act
RFETS	Rocky Flats Environmental Technology Site
TLV	Threshold Limit Value
TRU	Transuranic
VOC	Volatile Organic Compound
WAP	Waste Acceptance Plan
WIPP	Waste Isolation Pilot Plant
WSMS	Washington Safety Management Solutions
WWIS	WIPP Waste Inventory System

Technical Evaluation Report of WIPP Room-Based VOC Monitoring

1.0 Introduction

The WIPP HWFP establishes room-based limits for target VOCs in the air of rooms in individual disposal panels. This Technical Evaluation Report evaluates an alternative method of demonstrating compliance with the room-based VOC limits.

1.1 What are the Room-Based VOC Concentration Limits?

The room-based VOC limits are in Module IV of the HWFP, and are shown in Table 1 below.

Compound	VOC Room-Based Concentration Limit (ppmv)
Carbon Tetrachloride	9625
Chlorobenzene	13000
Chloroform	9930
1,1-Dichloroethene	5490
1,2-Dichloroethane	2400
Methylene Chloride	100000
1,1,2,2-Tetrachloroethane	2960
Toluene	11000
1,1,1-Trichloroethane	33700

ppmv (parts per million by volume)

Table 1 Room-Based VOC Concentration Limits
(from Table IV.D.1 of the HWFP)

The average concentration of the target VOCs in the air within an individual disposal room in an active panel must be less than the concentration limits in Table 1 above, even if some containers in the disposal room exceed the room-based concentration limits. The room-based limits were generated as a necessary component of the Resource Conservation Recovery Act (RCRA) Part B Permit Application, since the waste emplaced in WIPP would be emitting VOCs during the WIPP operational phase. To satisfy the requirement of no-migration, meaning that hazardous constituent concentrations shall not exceed those associated with agency-approved human health-based levels (HBLs) beyond the boundary of the disposal unit, an analysis was performed to determine chronic exposure levels for the public and surface WIPP workers as receptors. Points of compliance were determined, VOC concentrations at the points of compliance calculated for various average VOC level source terms, and a comparison to the HBL at each compliance point to the calculated VOC levels observed. Using the data from the

Idaho National Environmental Engineering Laboratory (INEEL) 930 drum data set where weighted average container headspace VOC levels were projected for 28 VOCs for mixed waste destined for WIPP, the VOC levels at the compliance points were determined and found to be well within the HBLs of 1 in 1×10^6 for type A and B carcinogens and 1 in 1×10^5 for type C carcinogens, and within the Occupational Safety and Health Administration (OSHA) time weighted average exposure limits for non-carcinogens. The greatest health-based risk from VOCs was found to be to a surface worker when the point of compliance was in the downstream flow just outside the exhaust shaft. Maximum average container headspace concentrations were determined and the maximum permissible exposures were calculated in accordance with EPA's public risk policy. The analysis set the maximum VOC levels in a room at EPA acceptable exposure levels. NMED recalculated the maximum VOC levels that met EPA acceptable exposure levels. NMED determination reduced the maximum VOC levels in a room for chlorobenzene and toluene to the lower explosive limit and 1,2-dichloroethane and 1,1,1-trichloroethane to the Immediately Dangerous to Life and Health (IDLH), all of which were less than the calculated values to meet EPA acceptable exposure levels. These maximum average container headspace concentrations determined by NMED are the room-based limits.

1.2 Methods of Determining Compliance with the Room-Based VOC Limits

Currently, there are two methods described in the HWFP to demonstrate compliance with the room-based VOC concentration limits. The first method involves measuring and tracking the VOC concentrations in the headspace gas (HSG) of each container of transuranic (TRU) waste destined for WIPP. The second method involves measuring trace amounts of VOCs in the main exhaust drift of the WIPP underground. Each method is described in more detail in Section 2.2 below.

1.3 Development of a New Waste Analysis Plan for WIPP

A HWFP modification request (PMR) has been developed proposing a new waste analysis plan (WAP) for WIPP. Among other things, the new WAP PMR proposes to change the current practice of sampling and analyzing the headspace gas (HSG) of each container of TRU waste destined for WIPP to determine the concentration of VOCs.

1.4 Purpose of this Report

As proposed in the new WAP PMR, container-by-container HSG VOC measurements will no longer be made. In the absence of such container-specific VOC data, WIPP must utilize an alternative method to demonstrate compliance with the room-based VOC limits. This report provides information on an alternative VOC monitoring method to determine compliance with the room-based limits, and demonstrates how the alternative method protects human health and the environment.

2.0 Background Information

This section provides an overview of how the room-based VOC limits were derived, the occupational exposure risks that the room-based limits were designed to protect against, and describes the current methods of determining compliance with the room-based limits.

2.1 The 1996 RCRA Permit Application

In 1996 as part of the WIPP RCRA Part B Permit Application and the associated WIPP No-Migration Variance Petition, an assessment of the potential environmental and human health impacts associated with the waste emplacement was necessary. This assessment was to demonstrate that no hazardous constituents would migrate beyond the boundary of the disposal unit at levels in excess of acceptable agency approved human health-based standards for the constituents. Since VOCs in the emplaced waste would become entrained in the mine ventilation air and make their way to the surface, part of the 1996 application required an assessment of the risk associated with VOCs in the waste and a determination of controls on VOC emissions that was protective of the public, environment, and WIPP workers, both at the surface and in the underground. This section details the determination of the risk associated with the VOCs in the waste and the controls implemented to meet emission limits.

2.1.1 Estimate of VOC content of the TRU Waste Inventory (930 Drums)

As part of the RCRA Part B Permit Application in 1996 and the No-Migration Variance Petition an assessment of the potential VOC release rate from WIPP during the waste emplacement phase was required. The complete details of this assessment are contained in Appendix C2 of the WIPP RCRA Part B Permit Application, DOE/WIPP 91-005. To satisfy this requirement all HGS waste characterization data that were available in 1995 was assembled and a profile of the VOCs typically observed was determined. The only available data were from INEEL and Rocky Flats Environmental Technology Site (RFETS) and was comprised of a 930 drum data set that represented ten of the twelve waste matrix code groups, or as they are now referred to, final waste forms. The 930 drum data set reported 28 VOC HGS concentrations that represented the 28 most prevalent VOCs in the waste. The average HGS concentration value for each of the 28 VOCs was determined for each of the waste matrix code groups. A projected full WIPP VOC source term profile was calculated by first determining the weighted average HGS concentrations for 28 VOCs within each waste matrix code group. The weighted averages for a given VOC in each waste matrix code group were then summed to obtain a full WIPP source term for each VOC. The weighting factors were obtained by determining the fraction of the waste in a projected full WIPP that each waste matrix code group represented in the TRU Waste Baseline Inventory Report, Revision 3. The waste matrix code groups and the weighting factors used in the calculation of the waste matrix codes contribution to the full WIPP source term are displayed in the Table 2.

Waste Matrix Code Group	Weighting Factor
Combustibles	0.353
Filter	0.0148
Graphite	0.0043
Heterogeneous	0.222
Inorganic non-metal	0.0102
Lead/cadmium metal	0.0018
Salt waste	0.000852
Soils	0.00739
Solidified inorganics	0.194
Solidified organics	0.0012
Uncategorized metal	0.171
Unknown	0.00966
TOTAL	1.00

Table 2 Waste Matrix Codes and Weighing Factors

2.1.2 VOCs that Pose Health Risk at WIPP

The assessment that was performed on the 930 drum set included weighted average HGS concentrations projected for a full WIPP. A determination of the risk to the public and WIPP workers associated with the 28 VOC constituents was made. This assessment was required to satisfy both the WIPP RCRA Part B Permit Application and the No-Migration Variance Petition submitted to EPA. This assessment was completed even though the Land Withdrawal Act that established WIPP excluded WIPP from the No-Migration provision. The full assessment is contained in Appendix D13 of the WIPP RCRA Part B Permit Application, DOE/WIPP 91-005; the WIPP No-Migration Variance Petition, DOE/CAO-96-2160; and in comments from Steve Zappe, NMED, titled "NMED Calculations for VOC Concentrations in WIPP Underground HWDUs", 11/19/98. The assessment determined a risk, based on an EPA method risk score, that considered the type of risk, the toxicity, and the weighted average VOC concentration for each of the 28 VOCs. The risk scores allowed a ranking of the 28 VOCs as to their risk to the health of the public and WIPP workers. From the ranking and a determination of the VOCs that represented approximately 99 percent of the risk due to air emissions, target VOCs were selected as indicator VOCs that would be monitored for compliance of VOC emission levels. The target VOCs and the Room Based Limits are shown in Table 1 in Section 1.1 of this report.

2.1.3 VOC Exposure Scenarios at WIPP

During the RCRA permit application process, four general VOC exposure scenarios were evaluated by NMED, and environmental performance standards were established. The exposure scenarios and performance standards are summarized in the following table:

VOC Exposure Scenario	Environmental Performance Standards
1) Resident living at WIPP site boundary, <u>chronic</u> exposure to VOCs	<ul style="list-style-type: none"> • for carcinogens, total individual risk less than 10^{-6} • for non carcinogens, hazard index from exposure less than 1
2) WIPP non-waste surface worker, <u>chronic</u> exposure to VOCs	<ul style="list-style-type: none"> • for carcinogens, total individual risk less than 10^{-6} • for non carcinogens, hazard index from exposure less than 1
3) WIPP underground waste worker, <u>acute</u> exposure to VOCs from a roof fall in an <u>open</u> room	<ul style="list-style-type: none"> • concentrations of four VOCs immediately after a roof-fall less than the IDLH concentrations (1,1,1-trichloroethane, 1,2-dichloroethane, carbon tetrachloride, and 1,1,2,2-tetrachloroethane)
4) WIPP underground waste worker, <u>acute</u> exposure to VOCs from a roof fall in a <u>closed</u> room	<ul style="list-style-type: none"> • concentrations of four VOCs immediately after a roof fall less than the IDLH concentrations (1,1,1-trichloroethane, 1,2-dichloroethane, carbon tetrachloride, and 1,1,2,2-tetrachloroethane) • concentration of two VOCs in closed room less than the LEL concentration (toluene, and chlorobenzene)

Table 3 - WIPP VOC Exposure Scenarios Evaluated by NMED
 (Ref #1-NMED's Direct Testimony Regarding Regulatory Process and Imposed Conditions, 1999)

This Technical Evaluation Report considers Scenarios 1 and 2 to represent the risks that the current and proposed underground monitoring collectively are to be protective of with regard to the public and the workers. The report focuses on the two WIPP underground waste worker acute exposure scenarios, and the alternative method of demonstrating compliance with the room-based limits in the absence of container-by-container HSG measurements.

2.2 Two Scenarios for Acute VOC Exposure to Workers in Disposal Rooms

Revision 5.2 of the RCRA Permit Application was submitted to NMED on January 17, 1996. In response, NMED issued a Notice of Deficiency (NOD), and requested that the applicants evaluate two acute VOC exposure scenarios to underground waste workers (Ref #1-*Direct Testimony Regarding Regulatory Process and Imposed Conditions, 1999*).

The first acute VOC exposure scenario, involving a roof fall in an open room, is shown in Figure 1

Figure 1 - Acute VOC Exposure Scenario, Roof Fall in an Open Room
(Ref #1-NMED's *Direct Testimony Regarding Regulatory Process and Imposed Conditions, 1999*)

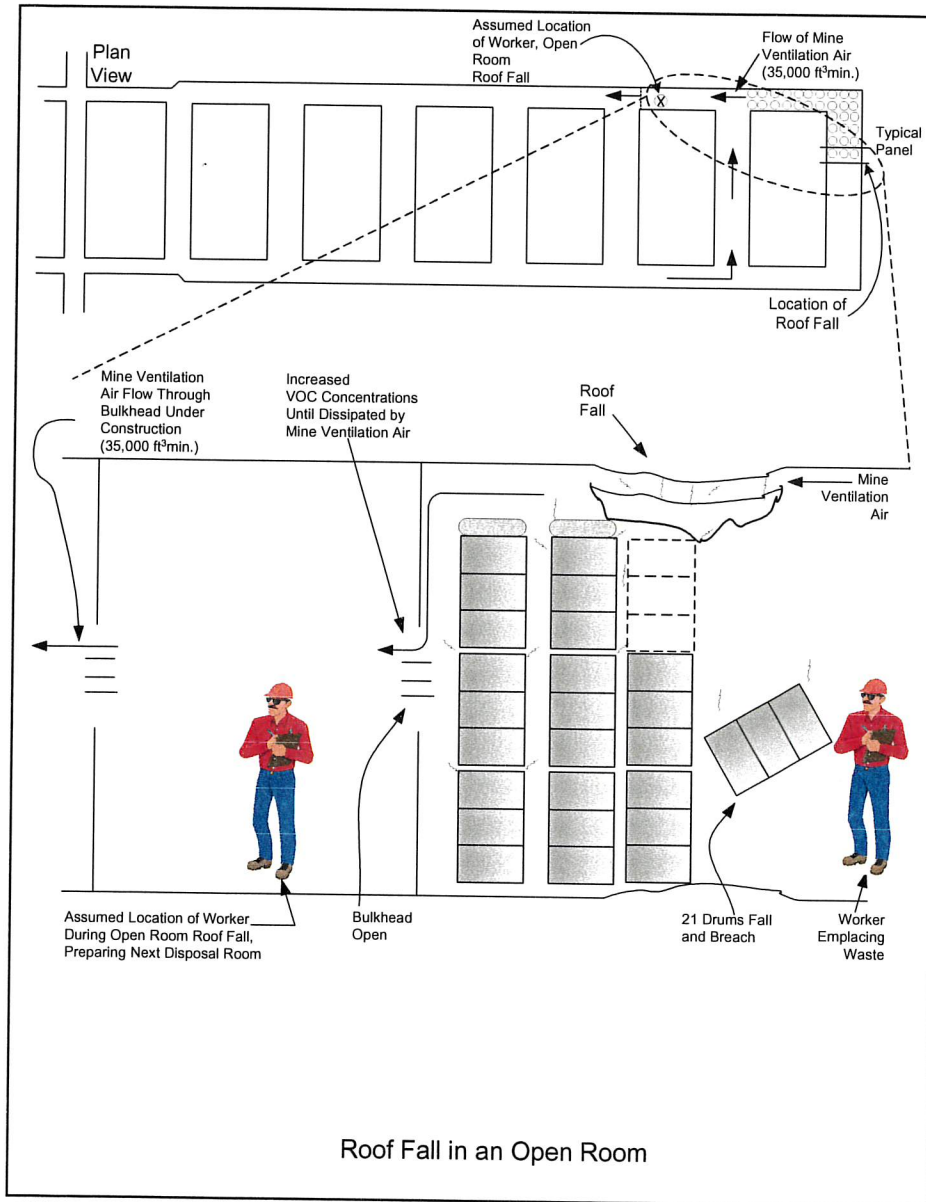


Figure 1 - Acute VOC Exposure Scenario, Roof Fall in an Open Room
 (Ref #1-NMED's Direct Testimony Regarding Regulatory Process and Imposed Conditions, 1999)

The second acute VOC exposure scenario, involving a roof fall in an closed room, is shown in Figure 2 below:

Figure 2 - Acute VOC Exposure Scenario, Roof Fall in a Closed Room
(Ref #1-NMED's Direct Testimony Regarding Regulatory Process and Imposed Conditions, 1999)(SIC)

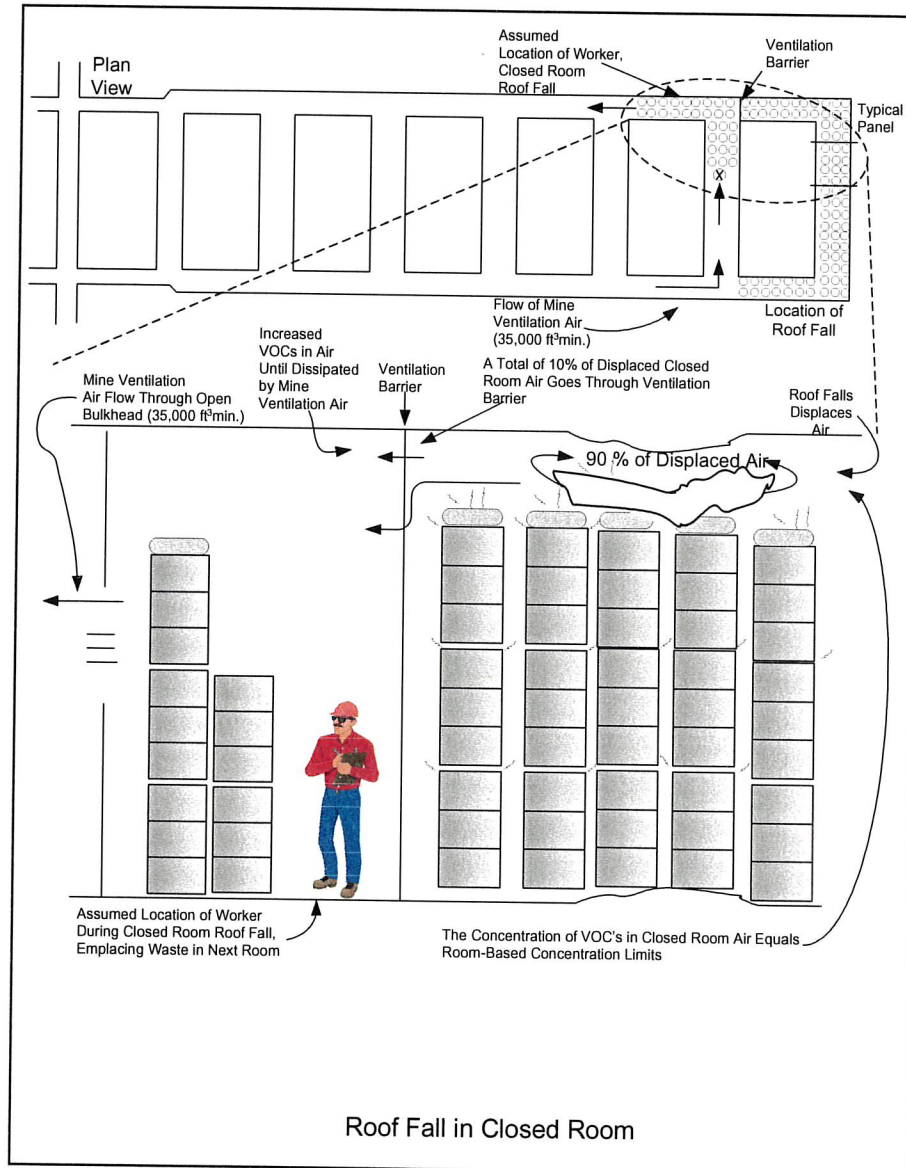


Figure 2 - Acute VOC Exposure Scenario, Roof Fall in a Closed Room
 (Ref #1-NMED's Direct Testimony Regarding Regulatory Process and Imposed Conditions, 1999)(SIC)

2.3 Current Methods of Determining Compliance with Room-Based VOC Limits

In evaluating WIPP's RCRA Permit Application In 1999, NMED determined that the environmental performance standards for protection of human health and environment from VOC releases to the air could be satisfied by maintaining the room-based VOC limits. There are two methods specified in the current HWFP for determining compliance with the room-based VOC limits.

VOC Exposure Scenario and Corresponding Environmental Performance Standard	Current Method of Determining Compliance
1) Resident living at WIPP site boundary, <u>chronic</u> exposure to VOCs: total carcinogen risk < 10^{-6} , and non-carcinogen exposure hazard index < 1	Confirmatory monitoring of trace amounts of VOCs in the main exhaust drift in the WIPP underground
2) WIPP non-waste surface worker, <u>chronic</u> exposure to VOCs: total carcinogen risk < 10^{-5} , and non-carcinogen exposure hazard index < 1	Confirmatory monitoring of trace amounts of VOCs in the main exhaust drift in the WIPP underground
3) WIPP underground waste worker, <u>acute</u> exposure to VOCs from a roof fall in an <u>open</u> room: concentrations of VOCs immediately after roof fall < IDLH	Tallying individual waste container HSG VOC measurements in the WIPP Waste Information System
4) WIPP underground waste worker, <u>acute</u> exposure to VOCs from a roof fall in a <u>closed</u> room: concentrations of VOCs in closed room < IDLH and <LEL	Tallying individual waste container HSG VOC measurements in the WIPP Waste Information System

Table 4 - Current Methods of Determining Compliance with Room-Based VOC Limits

2.3.1 Tracking VOC Concentrations in the Headspace Gas of Individual Containers

As provided in the current HWFP, container-by-container HSG VOC measurements are made and the data is entered into the WIPP Waste Information System (WWIS). The WWIS in turn is able to track and tally the average VOC HSG concentrations of containers emplaced within a particular disposal room at WIPP. This is the method used to determine compliance with the two specific environmental performance standards and those that protect underground waste workers against acute exposures to VOCs.

2.3.2 Confirmatory Monitoring of VOCs

The VOC Confirmatory Monitoring Program is designed to differentiate VOC concentrations attributed to open and closed panels from other potential sources. VOC monitoring confirms compliance with the HWFP VOC emission requirements. The only pathway for VOCs during the operational phase is via airborne transport. Any VOCs released in the underground facility would become entrained in the underground ventilation air and released to the atmosphere through the exhaust shaft. Any VOC emissions from emplaced waste pass by a monitoring system as they are directed to the exhaust shaft. Sources of VOC emissions, related to WIPP mine operational activities, also exist below ground surface. Fuel combustion, painting activities, cleaning solvents, and air conditioners are potential sources of VOCs.

Ambient air is monitored in the underground for the target compounds at two locations in the facility to quantify airborne VOC concentrations. VOC concentrations attributable to VOC emissions from open and closed panels containing transuranic mixed waste are measured by placing one VOC monitoring station just downstream from HWDUs at VOC-A and another station upstream from the open panel at VOC-B. In this configuration, VOC-B measures VOC concentrations attributable to releases from the upstream sources and other background sources of VOCs. VOC-A measures upstream VOC concentrations plus any additional VOC concentrations resulting from releases from the open panel and all closed panels. A sample is collected from each monitoring station on designated sample days. For each quantified target VOC, the concentration measured at VOC-B is subtracted from the concentration measured at VOC-A to assess the magnitude of VOC releases from closed and open panels.

The sampling locations were selected based on operational considerations. There are several different potential sources of release for VOCs. These sources include incoming air from above ground, facility support operations, open waste panels, and closed waste panels. In addition, because of the ventilation requirements of the underground facility and atmospheric dispersion characteristics, any VOCs that are released from HWDUs may be difficult to detect and differentiate from other sources of VOCs at any underground or above ground location further downstream of Panel 1. By measuring VOC concentrations close to the potential source of release (i.e., at Station VOC-A), it is possible to differentiate potential releases from background levels (measured at Station VOC-B).

The field sampling systems are operated in the pressurized mode. In this mode, air is drawn through the inlet and sampling system with a pump and then pumped into an initially evacuated SUMMA passivated canister by the sampler, which regulates the rate and duration of sampling. The passivation process forms a pure chrome-nickel oxide on the interior surfaces of the canisters. By the end of each sampling period, the canisters will be pressurized to about two atmospheres absolute. In the event of shortened sampling periods or other sampling conditions, the final pressure in the canister may be less than two atmospheres absolute.

3.0 New Information on VOCs in TRU Waste and Behavior of VOCs in the Repository

The 1995 VOC study was comprehensive, encompassing nearly 1000 drums (*Ref #2-Appendix C2*). Since that time a great deal of additional information has been collected, due to sites increasing their characterization efforts to enable shipment to WIPP. The characterization process has included developing compliant acceptable knowledge, as well as physically sampling nearly 100% of the shipped inventory HGS (the exceptions are those allowed by the WAP, which history shows that they underwent thermal processing which would eliminate the constituents of concern from the headspace. These containers have been statistically sampled according to the WAP requirements).

3.1 Headspace Gas Measurements Made since 1996

Three additional data sources have been developed after the initial study:

- WWIS data ranging from March 1999 to May 2003.
- 2,366 drums in an IT Corporation survey for Westinghouse TRU Solution of VOCs in drums at the RFETS that could impact hydrogen getters through poisoning by VOCs (*Ref #3-Parameters for Testing Impacts of VOCs as Poisons on Hydrogen Getter Performance*).
- 103 drums of IDC 003 RFETS waste at the INEEL that have been analyzed to determine hydrogen and flammable VOC content for shipment of this waste to WIPP (*Ref #4-IDC 003 Organic Setups Study*).

With the limitations of the initial data set, it is reasonable to re-evaluate the conclusions that were reached earlier regarding expected VOC levels in the WIPP repository. A new assessment of VOC levels in TRU waste using known currently available VOC data was performed by LANL (*Ref #5-Analysis of VOC Levels in the TRU Waste Inventory*). A waste inventory update was performed for the DOE Complex in 2003 in support of the WIPP Performance Re-certification Application (*Ref #6-Transuranic Waste Inventory Update Report 2003*). That inventory information provided the basis to project the expected VOC contributions by final waste forms (FWFs) from the waste that will be contained in a full WIPP repository.

The data from the three sources listed above were combined with data from the original 1995 study, with adjustments to remove sources of error. For example, because there was overlap in some of the data sets, potential bias that would have resulted from counting multiple results from a single drum was removed by using only the latest data from each drum. Data from drums that exceeded the mixture lower flammability limit for VOCs and hydrogen were excluded in accordance with WIPP requirements (*Ref #7-TRUPAC-II Authorization Methods for Payload Control*), because these drums could not be shipped to WIPP. Data that was collected less than 30 days after venting was excluded, in accordance with WIPP requirements (*Ref #8-Examination of Roof Collapse Scenario*). Analytical issues were resolved in a WIPP-compliant manner; data at or below the method detection limit was used at one-half the method detection limit (MDL) and data were eliminated if the corresponding blanks were contaminated. Also, the same screening process was applied to the original 1995 data set, so that meaningful comparisons could be made. Full details are reported in the LANL report.

3.1.1 Less VOCs in the TRU Waste Inventory than Originally Estimated

Using the much larger population of HSG samplings a new weighted average VOC source term for 28 VOCs was determined. VOC concentration measurements decreased significantly with respect to their previously projected values. The principal VOCs that contribute to the new source term have been reduced in number from three in the 1995 data to two in the new data set. These dominant VOCs, 1,1,1-trichloroethane and carbon tetrachloride, showed decreases in their weighted average concentrations to one-third and one-half of the 1995 values, respectively. All VOCs decreased to less than half of their 1995 values, with methylene chloride decreasing to only 2 percent of the 1995 projection. The full results are reported in the LANL study.

3.1.2 A Small Amount of TRU Waste Inventory Contributes Most of the VOCs

An examination of the data shows that one FWF contributes most of the VOC source term (the 1995 study showed three FWFs had significant contributions). The FWF responsible for the overwhelming majority of the source term is solidified organics. Although the current data set only contains information from RFETS and INEEL, all of the material in the study originated from RFETS. While this is a limitation, it represents a bounding case because solidified organics from DOE Hanford Site and LANL are not expected to contain higher concentrations of VOCs.¹ According to projections based on the 2003 inventory update, the majority of the solidified organics indicates that only four sites contain the bulk of the problem. The large sites are RFETS, INEEL, LANL, and Hanford (ETEC and LLNL having only about 13 m³ total). The solidified organic FWF represents approximately one percent of the total inventory, with the fraction originating from RFETS and INEEL, accounting for less than 0.5 percent.

3.1.3 The 1996 RCRA Permit Appendices were Conservative but Remain Valid

As reported previously in Section 2.1, an assessment was made in 1996 of the potential environmental and human health impacts of VOCs associated with waste emplacement. This was done in support of the WIPP RCRA Part B Permit Application and the No-Migration Variance Petition. The assessment was to show that even at very high VOC concentrations in a room, the room-based limits, the exposure levels at the surface for two chronic exposure scenarios were well within acceptable levels for no migration of hazardous contaminants. By limiting average VOC levels in a room to the room-based limits a conservative approach was implemented that would keep WIPP VOC emissions far below acceptable exposure levels.

Verification that WIPP remained in compliance was accomplished by environmental monitoring in the E300 exhaust drift at S1300, a point downstream of all the panels. The assessment was based on the VOC data available at the time, a 930 drum set at the INEEL. The data set included HSG data for all but two of the waste matrix code groups although the drum count in any group was generally less than 100 drums. The VOC averages by waste matrix code group in this data set clearly showed that there were very few cases where the room-based limits for a VOC could have been exceeded. In the risk assessments made using this VOC data, a number of conservative assumptions were made on the movement of VOCs from the drum headspace to the room air. Because of the small number of data points in a waste matrix code group, a conservative approach was taken to ensure that the room-based limits would not be exceeded.

The data set for a 2003 assessment of VOCs in DOE waste includes approximately 45,000 drums representing about 5 percent of the full WIPP volume. All but the soils waste matrix code group is included in this assessment. The results represent at least 2000 data points in each waste matrix code group except solidified organics. The data also demonstrate that average VOC levels have declined significantly for waste matrix code groups except solidified organics. The VOC with average concentrations exceeding the room-based limit in any waste matrix code group was carbon tetrachloride and that was only in solidified organics. Solidified organics makes up, at most, about one percent of the total waste destined for WIPP, and less than one-half of the solidified organics waste matrix code group or about 3000 drums contain high levels of carbon tetrachloride. With the current available data, the conservative approach taken in

¹ The solidified organics from INEEL and RFETS came from a process known as Oil and Solvent Immobilization System (OASIS). In the OASIS process a mixture of approximately 25 vol% cutting oil and 25 vol% solvents (mostly carbon tetrachloride and 1,1,1-trichloroethane) was mixed with 50 vol% Gypsum cement. This represents close to the theoretical limit of solvents that can be immobilized without giving rise to free liquids. Other methods such as the use of clay absorbents or vermiculite, typically are used to immobilize <25 vol% of solvents.

1996 is no longer the prudent approach since there does not appear to be sufficient inventory of high VOC concentration waste to fill a room. Even using the conservative assumptions from 1996 for VOC movement, the room-based limit can not be reached even if all the problem VOC waste from solidified organics were to be emplaced in a single room (*Ref #9-Statistical Analysis of VOC Levels in the TRU Waste Inventory*).

3.1.4 Compound Risk Assessment

A statistical analysis was performed on the HSG analyses that have been performed to date to determine which target compounds listed in the HWFP represent 99 percent of the risk. The methodology that was used in the WIPP RCRA Part B Permit Application Appendix D-13 was used to evaluate the new headspace analytical data. The results of this analysis are reflected in the following table (*Ref#9-Statistical Analysis of Volatile Organic Compounds in Transuranic Waste*).

Risk Class	VOC	Molecular Weight	Headspace Gas Concentration (ppm)	Headspace Gas Concentration (per m ³)	Unit Risk (m ³ per microgram)	Score	Percent
Carcinogens	Benzene	78.11	2.01	6421	0.00000830	0.05329039	0.42
	Bromoform	252.77	1.60	16539	0.00000110	0.01819308	0.14
	Carbon tetrachloride	153.84	72.8	458003	0.00001500	6.87005178	53.6
	Chloroform	119.39	2.52	12304	0.00002300	0.28298566	2.21
	Methylene chloride	84.94	6.75	23447	0.00000047	0.01102001	0.09
	1,1-Dichloroethylene	96.95	2.09	8286	0.00005000	0.41431648	3.23
	1,2-Dichloroethane	98.96	1.71	6920	0.00002600	0.17992738	1.40
	1,1,2,2-Tetrachloroethane	167.86	1.68	11533	0.00005800	0.66888675	5.22
	Tetrachloroethylene	165.85	1.75	11869	0.00000058	0.00688414	0.05
	1,1,1-Trichloroethane	133.4	49.1	267858	0.00001600	4.28573590	33.4
	1,1,2-Trichloroethane	133.42					
	Trichloroethylene	131.4	2.31	12413	0.00000170	0.02110204	0.16
	Vinyl chloride	62.5					
Non-Carcinogens	Carbon disulfide	76.14					
	Chlorobenzene	112.56	1.77	8.1	0.00000830	0.00006762	13.3
	(cis)-1,2-Dichloroethylene	96.95	1.74	6.9	0.00000830	0.00005726	11.3
	Isobutanol	74.12					
	Methyl ethyl ketone	72.1	10.9	32.1	0.00000830	0.00026675	52.6
	Toluene	92.13	3.70	13.9	0.00000830	0.00011570	22.8
	Trichlorofluoromethane	137.38					

Table 5 Calculation of Risk Contribution
From *Statistical Analysis of Volatile Organic Compounds in Transuranic Waste*.

3.2 Experimental Closed Room Monitoring in Panel 1

In 2001 a task team began meeting to determine a way to eliminate HSG sampling from the HWFP while maintaining compliance with the HWFP. The group decided that collecting samples inside the closed room environments might provide empirical data that would be of value in a future permit modification process.

The current VOC monitoring system was tested to determine if the system could detect releases of VOCs from the panel area. This test involved the release of a known gas in Panel 1 while collecting ambient air samples at VOC-A and VOC-B. The results indicated that VOC concentrations emitted from open and closed panels could be detected by the system in place (*Ref #10-VOC Test Release Report*).

An additional test was performed by the Carlsbad Environmental Monitoring and Research Center to determine if the long lengths of tubing necessary to perform this sampling would pose problems with the analysis of samples collected through the tubing. The test indicated that the long lengths of tubing would not cause significant impact to sample quality (*Ref #11-Silicosteel Tubing Evaluation*).

3.2.1 Apparatus and Methods

Sampling for VOCs in closed-room environments began on August 29, 2001 in Room 7 of Panel 1. The sampling method and procedures were adopted from the established Confirmatory VOC Monitoring Program. As ventilation barriers were installed, siliconized stainless steel tubing was installed at the exhaust side of the room. A manifold consisting of the siliconized stainless steel tubing was designed and constructed to create three sample inlet points. Each of these sample points collected samples of the air in the closed room at different elevations to account for the settling of the different target compounds. The sample line was then connected to a sampling unit further down the exhaust drift. The location of the sampling unit was eventually installed at the same location that housed VOC-A. Dual particulate filters were installed close to the point at which the tubing connected to the sampling unit to prevent the salt and other particulates from entering the system. Figure 4 shows the sample locations during the closed-room sampling of Panel 1.

Additional sampling locations were operated during the life of Panel 1. These included an inlet location in Room 4, inlet and exhaust locations in Room 3, and an exhaust location in Room 2. The inlet side sample locations in Panel 1 did not include a manifold setup at the sample inlet point. All other aspects of the setup were the same as in Room 7. The components of the closed-room monitoring system were the same as are used in the Confirmatory VOC Monitoring Program as described in Section 2.3.2 of this report.

3.2.2 Results of VOC Measurements in Closed Rooms

Closed-room monitoring conducted in Panel 1 started in August 2001 and lasted through February 2003. EPA method TO-14 was used in the analysis of closed-room samples, this is the same analytical method as is used in confirmatory monitoring. Results were validated by VOC monitoring personnel using existing procedures. The data for the monitored rooms indicated that over time the VOC concentrations in the closed rooms, do build up to higher levels than are measured at VOC-A. The highest concentration measured in Panel 1 was in Room 7 for 1,1,1-Trichloroethane at a concentration of 450 parts per billion by volume (ppbv), which was very low considering the room-based limit for this compound is 33,700 ppmv.

3.2.3 Rank Order Correlation of Closed Room VOCs to HGS Data

Over time the concentrations began to rise in each room. Data collected in Panel 1 was compared to WWIS data on a room-by-room basis. A statistical analysis was performed on this data to decide if a correlation of the closed room data and the WWIS data existed. The Washington Safety Management Solution (WSMS) analysis produced the following information "Logic suggests that the VOC representing the most volume (in liters) placed in a room should be measured at the highest concentration in the air, with the next highest volume VOC being measured at lower concentrations in the air, and so on as VOC concentrations decrease. In Room 7, the four highest volumes of VOCs have the following rank order:

1. 1,1,1-Trichloroethane
2. Toluene
3. Methylene Chloride
4. Carbon Tetrachloride

Air monitoring measurements would be expected to show that, over time, 1,1,1-trichloroethane concentrations exceed those for toluene, which exceed those for methylene chloride, which exceed those for carbon tetrachloride. This also implies that we expect the nature of the rank order to be non-random. Figure 4 is a graph showing concentrations of all four VOCs listed above over time. The graph shows that 1,1,1-trichloroethane concentrations are consistently above those for toluene, which are above those for methylene chloride, and so forth.

Rank order correlation assumes that the results of experiments are random events. Examples of experiments could be the measurements of VOCs in the air. If, for example, we measure four VOCs in underground room air and their ranks are random, then there is a 25 percent chance (1 in 4) that any particular VOC will emerge as the highest concentration for a set of four measurements. The chance that a given VOC will rank as the number one constituent in air twice in a row is 1 in 16, with the likelihood of three or more "#1" rankings decreasing the more times we run the experiment, i.e. sample the air.

The probability that the VOCs will exhibit the same ABCD rank order in the drums as in the air simply by chance is 1 in 24. Obviously, a 1 in 24 chance is possible, occurring about four times out of every 100 sampling events, on average. The probability of this ranking occurring consecutively two or more times decreases rapidly as the experiment is performed over and over.

Figure 4 shows that VOC concentrations have been checked in Room 7 almost 50 times between 8/29/01 and 2/19/03, with 44 of these events measuring all four VOCs of interest. For convenience, we can call 1,1,1-trichloroethane "A", toluene "B", Methylene chloride "C", and carbon tetrachloride "D". Of the measurements shown in Figure 4, 39 exhibit the ABCD ordered ranking in the air monitoring samples, which matches exactly the rank order ABCD in the drum HSG measurements.

The probability of observing the ABCD order 39 times out of 44 sampling events is virtually zero. As a perspective, you are about a million times more likely to die in a tornado than to have this consistently ordered VOC result by chance. From this evidence, we conclude that the rank order of VOCs is not a random event; rather, it is a function of the most abundant VOCs that are contained in the drums in a particular underground room" (Ref #12-Draft Rank Order Correlation in Underground Air at the WIPP).

4.0 Proposed Method for Determining Compliance: Closed-Room Roof Fall

WIPP is proposing a monitoring system that will monitor VOC concentrations inside closed rooms. This sampling will provide an accurate evaluation of the accumulated VOCs that have the potential to be pushed past the ventilation barriers in the event of a roof fall. The monitoring system will allow for a real measure of worker protection and ensure that room based limits are not exceeded.

4.1 Closed-Room Exposure Scenario

The closed-room exposure scenario depicted in NMED's testimony shows that the workers downstream of the exhaust of open panels have the potential to be exposed to high levels of VOCs in the event of a roof fall in the adjacent closed room. The scenario assumes that ten percent of the VOC concentrations in the effected closed room are pushed past the ventilation barrier into the air stream. It also assumes that workers are in the exhaust at the time of the fall.

4.2 Closed-room VOC Monitoring

The proposed VOC monitoring will allow for the quantification of the VOC concentrations in the closed rooms of the remaining HWDUs in the underground. The monitoring, will in essence, take the place of HSG gas sampling at the generator sites. Headspace gas sampling is currently performed, in part, as a conservative control on the VOC release to the surface and to ensure that workers will not be subject to an acute VOC exposure in the event of a roof fall in the closed room adjacent to the open room. The monitoring approach offers an actual air composition analysis, which is the real hazard in the fall scenario depicted in NMED's testimony regarding regulatory process and imposed conditions. The HSG gas analysis indicates what is contained in the drums and not what is actually likely to be pushed out of the ventilation barrier during a roof fall. In the event that VOC concentrations reach the point in which they pose a hazard, actions will be taken to mitigate the situation. These levels and actions are discussed in the following sections.

4.2.1 Apparatus and Methods

The closed-room sampling consists of instrumentation capable of collecting a sample through tubing installed into the closed room. The instrumentation is industry standard real-time monitors or an acceptable laboratory method. The system is capable of providing quality data at desired detection levels. The sampling in closed rooms would take place in all rooms except room one in all panels to receive waste. Each closed room would be monitored until the following room has been closed. At this time, the monitoring in the previous room would cease and the newly closed room will be monitored.

4.2.2 Frequency of Sampling

The sampling frequency for closed-room sampling will be once every two weeks. During Panel 1 closed-room sampling, samples were initially collected twice each week. After reviewing the data that was received from these samples, it was determined that sampling once every two

weeks per sampling location would be sufficient. The data did not indicate the closed room environment was changing quickly enough to warrant more frequent sampling, figure 3 shows this gradual rise. In the event that higher concentrations of VOCs are detected, a more frequent sampling interval can be incorporated.

4.3 Action Levels

One action level exists for the closed-room monitoring system. It is listed in Table 6. The action level is 95 percent of the room-based limits specified in the HWFP. It was determined that 95 percent of the room-based limits would be a sufficient level at which to begin the remedial action by evaluating the gradual rise of VOC concentrations in Room 7 of Panel 1. The gradual concentration rise in Room 7 of Panel 1 along with the relatively short time frame to complete the remedial actions, provide confidence in the action level. Remedial action is detailed in Section 4.4 of this report.

Compound	Action Level in ppmv
Carbon tetrachloride	9,145
Chlorobenzene	12,350
Chloroform	9,433
1,1-Dichloroethene	5,215
1,2-Dichloroethane	2,280
Methylene Chloride	95,000
1,1,2,2-Tetrachloroethane	2,812
Toluene	10,450
1,1,1-Trichloroethane	32,015

Table 6 Closed Room Action Level

4.4 Actions to Mitigate Risk From High VOC Conditions

Upon receiving analytical results that indicate one or more of the compounds has reached a level that exceeds half of the action level, sampling frequency would increase to determine how fast the concentrations are rising. In the event that the VOC concentrations inside the closed room reach the action level, measures will be taken to mitigate the hazardous situation. If the condition rises to reach the 95 percent action level, another sample will be taken to confirm the existence of such a condition. If the second sample confirms that the room is at the 95 percent limit the current active room will be abandoned and two ventilation barriers, of the type shown in Figure 7, will be installed. This action scenario is shown in Figure 6. A typical (single layer) ventilation barrier is shown in figure 7.

5.0 Proposed Method of Determining Compliance-Open Room Roof Fall

For the active rooms of open panels real-time monitoring will take place to ensure worker safety in the exhaust of that panel. This monitoring will protect the workers from an acute release of VOCs in the event of a roof fall in an active room.

5.1 Open Room Exposure Scenario

In the event of a roof fall in accordance with the conditions outlined in HRM 98-04(P) New Mexico Environment Department's Direct Testimony Regarding Regulatory Process and Imposed Conditions, NMED is concerned about the formation of an IDLH atmosphere in the hypothetical event of a roof fall in an active room. In such a scenario, falling roof material breaches multiple drums, and releases a quantity of HSGs, which NMED considers may create an Immediately Dangerous to Life and Health (IDLH) concentration of VOC's in the breathing zone of a worker in the active room.

5.2 Open Room VOC Monitoring

To address such a scenario, WIPP proposes to provide a VOC monitoring system in the active room. This system will provide warning to underground workers, and opportunity for workers to evacuate the active room and exhaust drift, avoiding exposure in the event of VOC release.

5.2.1 Apparatus and Methods

WTS will use one or more multi-point continuous real-time monitoring systems in the active room and exhaust drift. The integrated systems are common in industry, and typically include the detection instrumentation, manifold, and control systems in a weather resistant enclosure, with tubing routed to the detection points. The systems also include integral or separate alarm enunciators, along with communications to a central monitoring facility. As the working location in the active room is the location of concern, and is continuously moving as containers are placed, it is anticipated the real-time monitoring systems to be skid or trailer mounted, located near the emplacement face, and to migrate as necessary with the emplacement face to minimize sample tubing length. Stationary sample points will be maintained through the addition or relocation of sample tubing as systems are relocated. Sensor technology is capable of detection at the OSHA PEL for each of the compounds of concern.

5.2.2 Frequency of Sampling

In order to provide timely warning to workers in the vicinity in case of a scenario such as a roof fall/container breach/VOC release, monitoring must be at least semi-real time, i.e. a detector or detector system running real time, and sampling a discrete number of sample points in sequence.

5.3 Action Levels

Table 7 lists the action levels for the VOC's of concern within occupied workspace (the active room and exhaust drift). It is an accepted and conservative industrial hygiene practice to select either the American Conference of Governmental Industrial Hygienist's (ACGIH) Threshold Limit Values (TLV's) or OSHA PEL's, whichever is lower. This assures regulatory compliance, and addresses health based concerns that may not be immediately addressed by regulation. WIPP provides an additional safety factor by treating the ACGIH TLVs and OSHA PELs 8-hour time weighted exposure values as ceilings. By evacuating workers from the area of concern immediately should TLV or PEL concentrations occur, WIPP effectively assures that workers' cumulative exposures will not approach occupational exposure limits of concern.

VOC of Concern	NIOISH IDLH – ppmv	OSHA 8-hr PEL - ppmv	ACGIH TLV - ppmv	WIPP Action Level - ppmv
Carbon Tetrachloride	200	10	5	5*
Chlorobenzene	1000	75	10	10*
Chloroform	500	50 (ceiling)	10	10*
1,1-Dichloroethene	Not established	Not established	5	5*
1,2-Dichloroethane	50	50	10	10*
Methylene Chloride	2300	25	25	25
1,1,2,2-Tetrachloroethane	100	5	1	1*
Toluene	500	200	50	50
1,1,1-Trichloroethane	1000	350	Not listed	350

Table 7. WIPP Action Levels for Evacuation of the Active Room and Exhaust Drift

*Action level based on the current ACGIH TLV (8-hour TWA)

5.4 Actions Taken to Mitigate High VOC Conditions

In the event of a roof fall and subsequent VOC release in the active room, the prudent course of action is to evacuate that room and the exhaust drift pending evaluation of the event. In the unlikely event that airborne VOC concentrations remain at levels at or above the applicable OSHA PEL's, active room ventilation shall be adjusted to provide sufficient dilution to maintain VOC levels beneath those PEL's.

6.0 Conclusions Regarding Proposed New Methods of Determining Compliance

WIPP concludes that the methods proposed to monitor the open panel for VOCs offer a safer, more effective method for determining compliance with the HWFP for room-based limits. In addition to this worker safety will be enhanced with new technology. The proposed methods will offer the facility a better protection from and understanding of VOC concentration that are being emitted from the waste containers within a closed room.

6.1 Effectiveness

The above monitoring strategy addresses worker exposure as the result of a sudden event within either a closed room or the active room. In case of an event of sufficient magnitude to generate significant VOC concentrations, Real-time monitoring, coupled to an alarm system, is an effective way to ensure that personnel are alerted to evacuate in a timely manner. A VOC monitoring system provides demonstrable sensitivity, repeatability, response time, alarm

capabilities, and system status surveillance, which in turn provides assurance that personnel will be alerted in case of VOC release.

6.2 Technical Validity

Sampling methods to be used in the monitoring of the closed and open rooms will be approved and accepted laboratory and industrial standards. The monitoring of the locations will provide reliable information on the actual risk to the workers. Additional VOC monitoring in the adjacent closed room to the active room and continuous VOC monitoring of the active room are more proactive and sufficient approaches to remaining compliant on VOC emissions from WIPP and are considerably more protective of personnel in the underground.

WIPP has chosen the action levels for VOC exposures in the underground based on accepted health-based consensus standards for occupational exposure to hazardous materials in the workplace, OSHA PELs, and the capabilities and limitations of available detection technology.

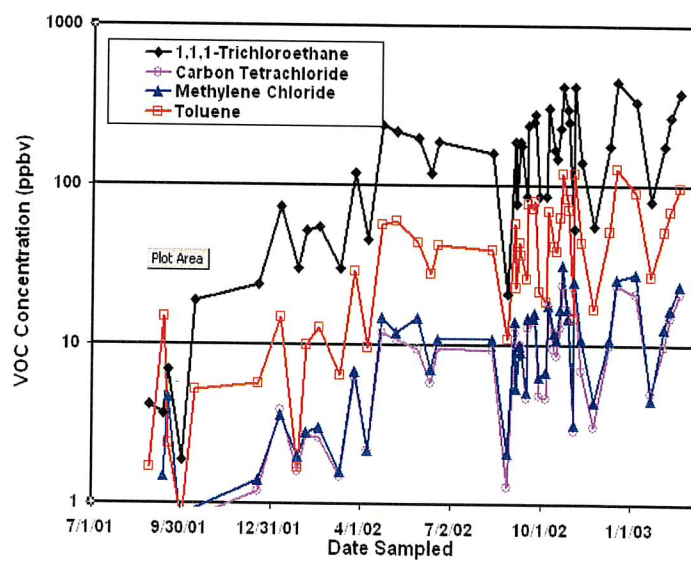
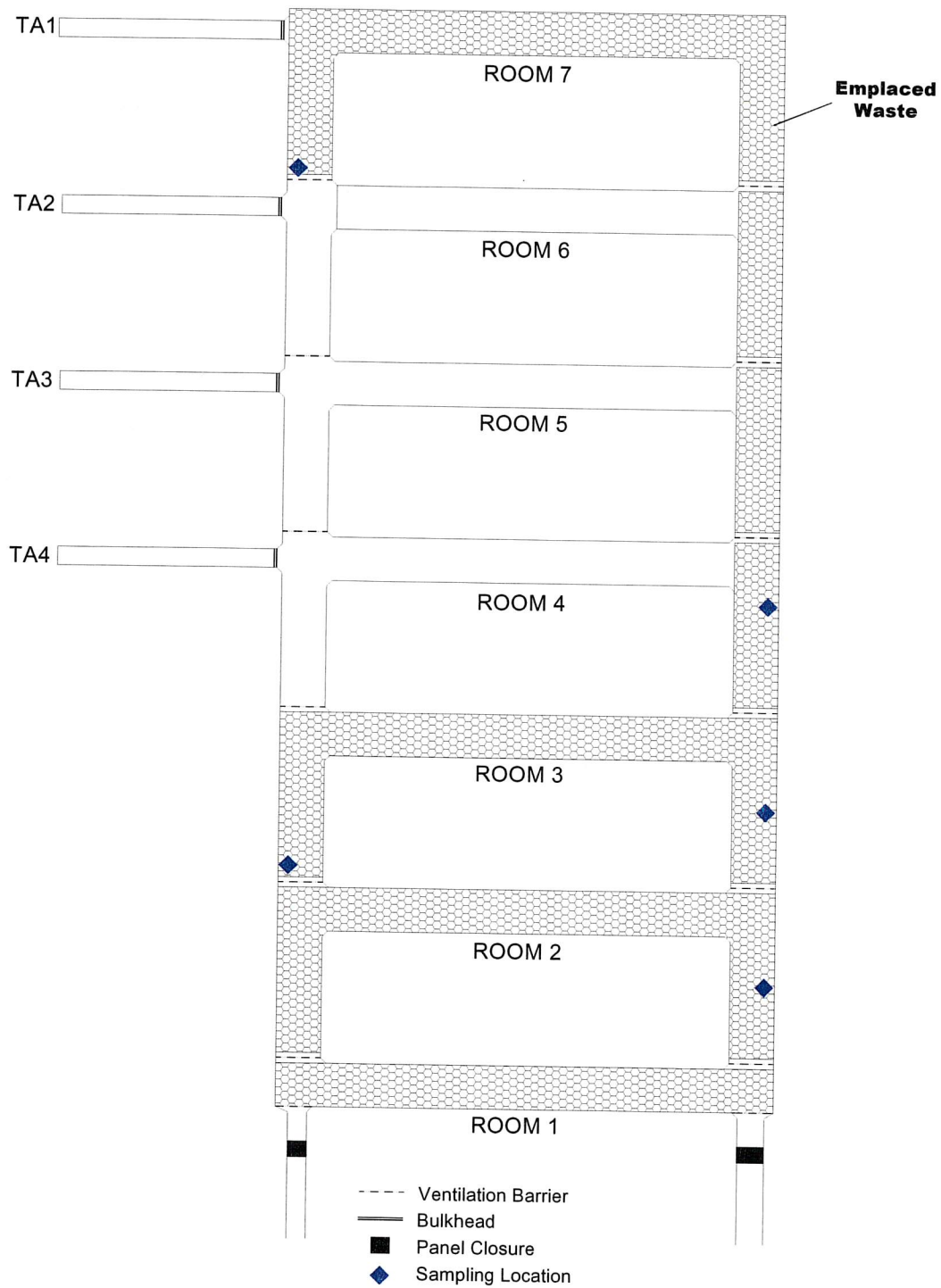


Figure 3

Room 7/WWIS Time Series Plot (Ref #12-Draft Rank Order Correlation in Underground Air at the WIPP)

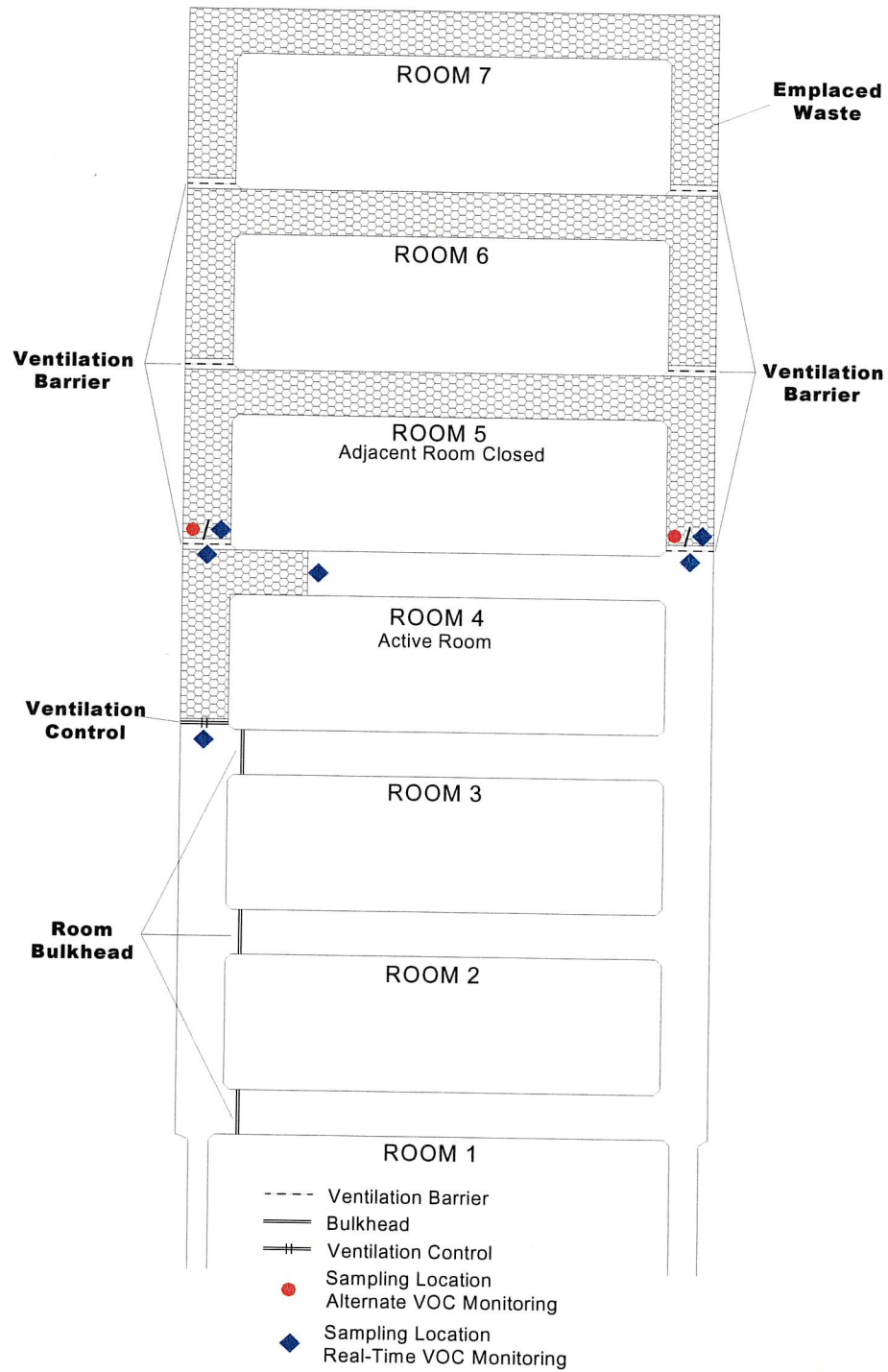


**PANEL 1
CLOSED ROOM
SAMPLING LOCATIONS**

For Illustrations Purposed Only

Figure 4
Panel 1 Closed Room Sampling Locations

Typical Disposal Panel



CLOSED AND ACTIVE ROOM VOC MONITORING

For Illustrations Purposed Only

Figure 5 Closed and Active Room Monitoring Locations

CLOSED ROOM ISOLATION

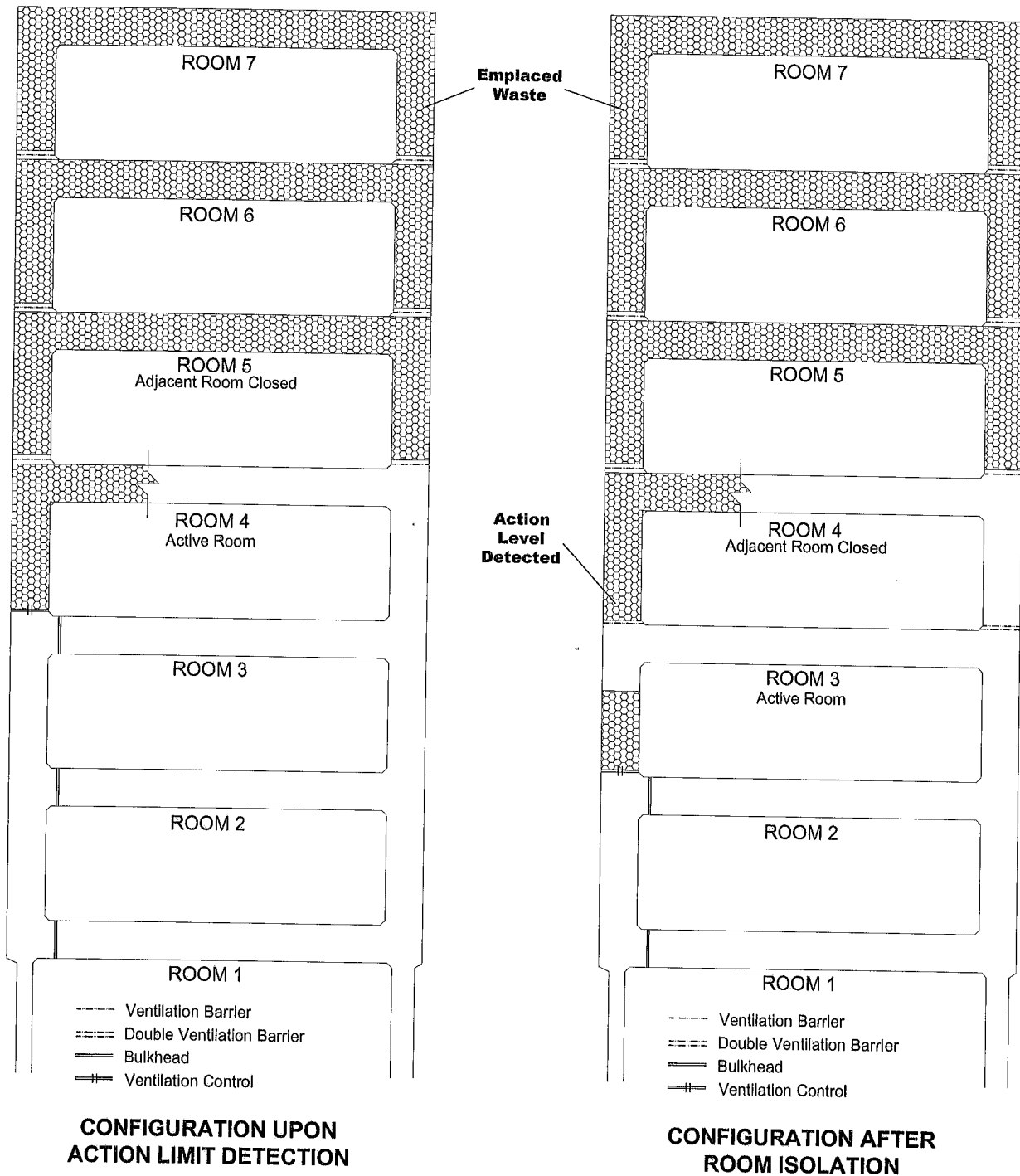


Figure 6 Action for Closed Room

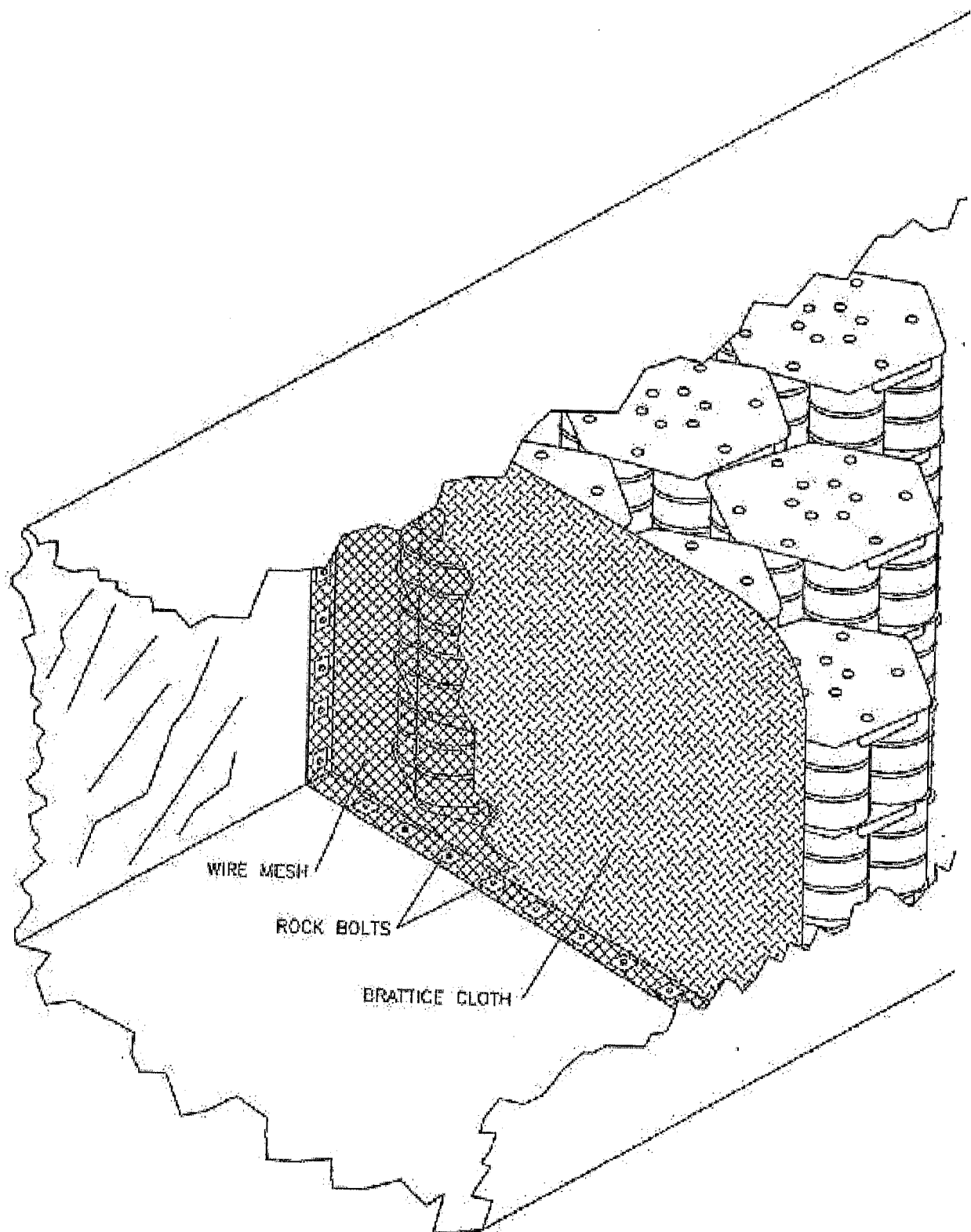


Figure 7
Typical Ventilation Barrier

Figure 4
Panel 1 Closed Room Sampling Locations

Figure 5 Closed and Active Room Monitoring Locations

Figure 6 Action for Closed Room

Figure 7
Typical Ventilation Barrier

References

- 1) New Mexico Environment Department, Direct Testimony Regarding Regulatory Process and Imposed Conditions, 1999
- 2) WIPP RCRA Part B Permit Application, DOE/WIPP 91-005, Revision 5, APPENDIX C2, Data Accumulated from Headspace-Gas Analysis
- 3) IT Corporation generated for Westinghouse TRU Solutions, "Parameters for Testing Impacts of VOCs as Poisons on Hydrogen Getter Performance", May, 2001
- 4) IDC 003 Organic Setups Study, INEEL, 2001, private communication M. J. Connolly
- 5) LA-UR-03-5393, W.R McCulla and G.D. Van Soest, "Analysis of VOC Levels in the TRU Waste Inventory,".
- 6) LA-UR-03-3427 "Transuranic Waste Inventory Update Report, 2003", June, 2003
- 7) TRAMPAC/REV.19b, "TRUPAC-II Authorization Methods for Payload Control, TRAMPAC, March, 2003
- 8) WIPP RCRA Part B Permit Application, Attachment 1 "Examination of Roof Collapse Scenario", DOE/WIPP 91-005, Revision 6
- 9) Jeff Meyers, Statistical Analysis of Volatile Organic Compound Levels in Transuranic Waste, August 22, 2003.
- 10) Bill McCulla, VOC Test Release Report, 2001 (e-mail report to S.Kouba)
- 11) Arimoto, Schloessin, McCulla, Sage, Silicosteel Tubing Evaluation, September 2002
- 12) Jeff Meyers, Draft Rank Order Correlation in Underground Air at the WIPP

Technical Paper:
An Analysis of TRU Waste Characterization Accuracy

Bob Kehrman
Wille Most

September 3, 2003

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Executive Summary

The Waste Isolation Pilot Plant (WIPP) Hazardous Waste Facility Permit (HWFP) prescribes waste characterization information that must be collected for every container of transuranic (TRU) that is to be disposed of at the WIPP facility. In addition, the HWFP requires that this information be confirmed through sampling and analysis and waste examination. This paper provides ten different metrics for determining the accuracy of waste characterization. These are as follows:

1. Waste Matrix Code (WMC) Assignment
2. Waste Stream Assignment
3. Toxicity Characteristic Assignment based on base material identification
4. F-listed Solvent Assignment based on headspace gas sampling and analysis (HSGSA)
5. Toxicity Characteristic volatile organic compounds (VOCs) and non-toxic F003 Assignment based on HSGSA
6. Toxicity Characteristic Assignment to a S3000 or S4000 Waste based on solids sampling and analysis (SS)
7. Toxicity Characteristic VOCs and non-toxic F003 Assignment based on SS
8. F-listed Solvent Assignment based on SS
9. Hazardous Waste Number (HWN) Assignment
10. Unexpected Prohibited Items

Overall statistics were compiled based on containers of waste that were characterized and confirmed since the HWFP was put into effect in October 1999.. These are tabulated in Table 1.

Table 1 Overall Results of Waste Characterization Accuracy

METRIC	NUMBER OF CONTAINERS	RESULT (AK ACCURACY)
1. Waste Matrix Code Assignment	47, 213	98.5%
2. Waste Stream Assignment		
3. Toxicity Characteristic Assignment	44, 402	99.99%
4. F-listed Solvent Assignment (HSGSA)	39,021	97%
5. Toxicity Characteristic VOCs and Non-toxic F003 Assignment (HSGSA)	39,021	100% (66.5%) Note 1
6. Toxicity Characteristic Assignment to an S3000 or S4000 Waste (SS)	25,336	97.06%
7. Toxicity Characteristic VOCs and Non-toxic F003 Assignment (SS)	25,336	100%
8. F-listed Solvent Assignment (SS)	25,336	100%
9. Hazardous Waste Assignment	17,814	99.05%
10. Unexpected Prohibited Items	43, 649 (Radiographed) 535 (Visually examined)	99.99%

Note 1: The AK accuracy result in parenthesis represents the INEEL practice of assigning toxicity characteristic codes based on HSGSA only, absent the confirmatory data from SS as required by the HWFP

To date, there are ten waste streams where HSGSA resulted in the assignment of a new F-listed HWN after it was characterized based on acceptable knowledge (AK) information. This affected 1,202 containers of waste. All of the HWNs added were allowed by the HWFP. **The addition of the HWNs did not change the sampling and analysis or the way in which the waste stream was handled.**

In the case of the homogeneous solids waste stream, there was one instance when SS resulted in the addition of two characteristic HWNs, affecting 744 containers. In this case, the waste stream was already considered to be a mixed waste stream, containing both listed and characteristic waste. **Once again, the confirmation did not change the status of the waste stream, nor did it result in additional handling or management requirements.**

In other instances, INEEL added toxicity characteristic HWNs to waste streams based on HSGSA, even though these HWNs were not identified during SS on those waste streams that are homogeneous solids. This affected eight waste streams containing 13,808 containers. **The addition of the HWNs did not change the status of the waste stream, nor did it result in additional handling or management requirements.**

Overall, 5.0 percent of the waste containers had new HWNs assigned to them through the confirmatory process. In addition, other assignments have been conservatively made to numerous waste streams and individual containers. In no case did the assignments change the manner in which the waste was managed nor did it affect the disposal process. **There were no recorded instances where the results of HSGSA or SS resulted in the removal of a container from the generator sites' transuranic (TRU) waste inventory because it was determined to be unsuitable for disposal in WIPP.**

Cumulatively, generator sites have radiographed or visually inspected over 40,000 containers of waste. **The waste examination has shown that the AK information is very accurate, with a composite AK accuracy of 98.5 percent with regard to WMC or waste stream reassignments and with HWN reassignment based on the observation of base materials only occurring 0.15 percent of the time.**

The high accuracies dispel the belief that generator site waste characterization is inadequate and in need of confirmation using intrusive methods such as HSGSA and SS in order to safely manage the waste. In fact, there are no reported instances in all the containers sampled when HSGSA and SS resulted in different handling or disposal requirements. However, the lack of usefulness for HSGSA and SS does not eliminate the need to be diligent with the waste characterization process and to carefully verify waste characterization information. This can be done by implementing waste examination of a representative subpopulation of the waste at a prudent rate.

1.0 Waste Characterization Accuracy Metrics

The WIPP HWFP requires that AK information be used extensively for waste characterization. Specifically, according to the Waste Analysis Plan (**WAP**) in the HWFP (HWFP Attachment B, Section B-3b), AK information is used for the following:

- To delineate TRU mixed waste streams
- To assess whether TRU mixed heterogeneous [SIC] debris wastes exhibit a toxicity characteristic (20.4.1.200 NMAC, incorporating 40 CFR §261.24)
- To assess whether TRU mixed wastes are listed (20.4.1.200 NMAC, incorporating 40 CFR §261.31)

Although not explicitly in the list of AK information uses, the HWFP requires that the AK documentation must include information demonstrating that a generator site had in place at the time the waste was generated: *Procedures describing management controls used to ensure prohibited items (specified in the WAP, Permit Attachment B) are documented and managed* (HWFP Attachment B, Section B4-2b)

The HWFP further requires confirmation of information generated through the AK process (WIPP Hazardous Waste Facility Permit Attachment B, Section B-4a(1), emphasis added):

The waste characterization data obtained through WAP implementation will be used to ensure that the Permittees meet regulatory requirements with regard to both regulatory compliance and to ensure that all TRU mixed wastes are properly managed during the Disposal Phase. To satisfy the RCRA regulatory compliance requirements, the following DQOs are established by this WAP:

- Headspace-Gas Sampling and Analysis
 - To identify VOCs and quantify the concentrations of VOC constituents in the total waste inventory to ensure compliance with the environmental performance standards of 20.4.1.500 NMAC (incorporating 40 CFR, §264.601(c)), **and to confirm hazardous waste identification by acceptable knowledge.**
- Homogeneous Waste Sampling and Analysis
 - To compare [90 percent upper confidence limit] **UCL₉₀** values for the mean measured contaminant concentrations in a waste stream with specified toxicity characteristic levels in 20.4.1.200 NMAC (incorporating 40 CFR §261), to determine if the waste is hazardous, **and to confirm hazardous waste identification by acceptable knowledge.**
 - To report the average concentration of hazardous constituents in a waste stream, as specified in 20.2 [SIC].1.200 NMAC (incorporating 40 CFR §261) Appendix VIII, with a 90 percent confidence interval, with all averages greater than Program Required Quantitation Limit (**PRQL**) considered a detection and subsequent assignment of the waste (if an adequate explanation for the constituent cannot be determined) as a hazardous waste, **and to confirm hazardous waste identification by acceptable knowledge.**

- Radiography

- To verify the TRU mixed waste streams by Waste Matrix Code [WMC] for purposes of physical waste form identification and determination of sampling and analytical requirements, to identify prohibited items, **and to confirm the waste stream delineation by acceptable knowledge.**

- Visual Examination

- To verify the TRU mixed waste streams by Waste Matrix Code for purposes of physical waste form identification, determination of sampling and analytical requirements, and to identify prohibited items.
- **To provide a process check on a sample basis by verifying the information determined by radiography, and to confirm the waste stream delineation by acceptable knowledge.**

Generator sites are required to determine their AK accuracy as a measure of the effectiveness of their AK program. The HWFP defines accuracy for AK as follows (HWFP Attachment B4, Section B4-3e)):

- **Accuracy** - Accuracy is the degree of agreement between an observed sample result and the true value. The percentage of waste containers which require reassignment to a new waste matrix code and/or designation of different hazardous waste codes based on the reevaluation of acceptable knowledge or on obtaining sampling and analysis data will be reported as a measure of acceptable knowledge accuracy.

The requirement to measure and report AK accuracy is further clarified in HWFP Attachment B4-3e.

Each site shall address quality control by tracking its performance with regard to the use of acceptable knowledge by: 1) assessing the frequency of inconsistencies among information, and 2) documenting the results of acceptable knowledge confirmation through radiography or visual examination, headspace-gas analyses, and homogeneous waste analyses. In addition, the acceptable knowledge process and waste stream documentation shall be evaluated through internal assessments by quality assurance organizations and assessments by auditors or observers external to the organization (i.e., DOE/Carlsbad Field Office (CBFO), NMED, EPA).

The HWFP, in Attachment B4, Section B4-3d, requires the measurement of AK accuracy. This requirement is implemented at each generator site through a CBFO-approved TRU waste characterization program. The determination of AK accuracy begins with the confirmation of AK information using waste examination or sampling and analysis.

Requirements for confirming AK information using waste examination (radiography or visual examination **(VE)**) follow. Note that the HWFP text is specific regarding those waste characteristics that are to be confirmed (emphasis added).

Acceptable knowledge characterization results shall be confirmed for both retrievably stored and newly generated waste. All retrievably stored waste shall be characterized using

radiography or visual examination to confirm the Waste Matrix Code¹ and waste stream² and certify compliance with the WAP (Permit Attachment B). If a site must repackage its retrievably stored waste, either the visual examination technique prior to or during waste packaging or radiography (or VE in lieu of radiography) after waste packaging shall be used to confirm acceptable knowledge information.

Potential toxicity characteristics for base materials that compose TRU mixed heterogeneous debris (S5000) waste may be determined without destructive sampling and analysis via acceptable knowledge.³ Sites will assign a Waste Matrix Code and waste stream to each container of waste using acceptable knowledge. In lieu of confirmatory sampling and analytical or other data to the contrary (including headspace gas and total/TCLP [Toxicity Characteristic Leaching Procedure] analysis of solids/soils), sites shall assign the toxicity characteristic hazardous waste codes based on the presence of the constituent identified by acceptable knowledge, regardless of the quantity or concentration.

Requirements for confirming AK information using HSGSA and SS follow. Note that the HWFP text is specific regarding those waste characteristics that are to be confirmed (emphasis added).

Headspace-gas sampling and analysis shall be conducted on all TRU mixed waste or randomly selected containers from waste streams that meet the conditions for reduced headspace gas sampling listed in Permit Attachment B, Section B-3a(1), to be sent to the WIPP facility. Headspace-gas data will be used to confirm the presence or absence of volatile organic compounds (VOCs) identified using acceptable knowledge.

The Permittees shall require sites to use acceptable knowledge to identify spent solvents associated with each TRU mixed waste stream or waste stream lot. **Headspace-gas data will then be used to confirm acceptable knowledge concerning the presence or absence of F-listed solvents⁴ and concentration of applicable toxicity characteristic solvents⁵.** Sites shall confirm the assignment of F-listed hazardous waste codes (20.4.1.200 NMAC, incorporating 40 CFR §261.31) by evaluating the average concentrations of each VOC detected in container headspace gas for each waste stream or waste stream lot using the upper 90 percent confidence limit (UCL₉₀). The UCL₉₀ for the mean concentration shall be compared to the program required quantitation limit (PRQL) for the constituent. If the UCL₉₀ for the mean concentration exceeds the PRQL, sites shall reevaluate their acceptable knowledge information and determine the potential source of the constituent. Sites shall provide documentation to support any determination that F-listed organic constituents are associated with packaging materials, radiolysis, or other uses not consistent with solvent use. If the source of the detected F-listed solvents cannot be identified, the appropriate spent

¹ This is AK accuracy Metric 1.

² This is AK accuracy Metric 2.

³ Though the text is not explicit, generator sites report changes to HWNs due to identification of base materials. For example if a radiography operator were to see a lead-lined glove in a container that does not carry the D008 HWN, the D008 HWN would be assigned to the container. This is reported in this paper as AK accuracy Metric 3.

⁴ This is AK accuracy Metric 4. The process for determining the presence is in the following sentence. Note that only the presence of an F-listed solvent in the headspace that is not expected based on the AK information is considered a discrepancy. That is, the absence of an F-listed solvent in the headspace gas sample is not a discrepancy.

⁵ This is AK accuracy Metric 5. Note that the HWFP allows a characteristic toxicity HWN or a non-toxic F003 HWN to be deleted based on the results of HSGSA. This is not counted against AK accuracy in this paper since leaving the HWN does not change the manner in which the waste is managed, even if the waste becomes a non-mixed waste as the result of the change.

solvent hazardous waste code will be conservatively applied to the waste stream. In the case of applicable toxicity characteristic VOCs and non-toxic F003 constituents, generator/storage sites may assess whether the headspace gas concentration would render the waste non-hazardous for those characteristics and change the initial acceptable knowledge determination accordingly.

Hazardous wastes associated with S3000 and S4000 waste streams will be verified based on the results of the total/TCLP analysis of a representative homogeneous waste sample.⁶ If discrepancies between the results obtained from homogeneous waste sampling and analysis and headspace-gas sampling and analysis exist (i.e., a VOC is detected in the solidified waste but not in the headspace), the most conservative results will be used to verify acceptable knowledge and assign hazardous waste codes, as applicable. As with headspace gas, if the total/TCLP results indicate that the concentration of a characteristic waste or non-toxic constituent of an F003 waste is below regulatory levels, the hazardous waste code assigned initially by acceptable knowledge may be changed as part of the confirmatory process.⁷ Otherwise, if an F-listed waste constituent is detected, the appropriate hazardous waste code shall be applied.⁸

These measures of AK accuracy are defined in this paper in terms of "Metrics" which assist in understanding the senselessness of the various confirmatory activities:

1. **WMC Assignment** is confirmed using radiography or VE. Each time a container is assigned a new WMC, the reassignment is recorded against AK accuracy.
2. **Waste Stream Assignment** is confirmed by radiography or VE. Each time a container is assigned to a different waste stream it is counted against AK accuracy.
3. **Toxicity Characteristic Assignment** is confirmed by determining if a base material is in a waste container through radiography or VE. The presence of the material in a container where it is not expected is counted against AK accuracy.
4. **F-listed Solvent Assignment** is confirmed using HSGSA. If the UCL_{90} concentration of an F-listed solvent exceeds the PRQL and the solvent has not been identified in the AK record, the HWN is added. The addition is counted against AK accuracy unless the presence of the solvent can be explained as a result of packaging or radiolysis.

⁶ This is AK accuracy Metric 6. Note that the permit uses "i.e." instead of "e.g." in the parenthetical statement in the following sentence in the citation. This defines a discrepancy for this metric as the situation where the compound appears in the solids sample and not in the headspace gas sample **and not vice-versa**. One site has reported the assignment of a toxicity HWN based on HSGSA results alone. That is, the solids sampling did not support the assignment. This is a conservative application of HWNs by the generator site. This discrepancy is reported in this paper; however, it is not counted against the AK accuracy since the assignment of a toxicity HWN using headspace gas analysis is not specifically required by the HWFP and is not required for regulatory compliance purposes.

⁷ This is AK accuracy Metric 7. Note that the HWFP allows a characteristic HWN or a non-toxic F003 HWN to be deleted based on the results of SS. This is not counted against AK accuracy in this paper since leaving the HWN does not change the manner in which the waste is managed, even if the waste becomes a non-mixed waste as the result of the change.

⁸ This is AK accuracy Metric 8.

5. **Toxicity Characteristic VOCs and non-toxic F003 Assignment** can be changed (deleted) based on headspace gas concentration measurements. Any change does not count against AK accuracy in this paper.
6. **Toxicity Characteristic Assignment to an S3000 or S4000 Waste** is confirmed by solids sampling and TCLP/totals analysis. If a VOC is detected in the solids portion but not in the headspace and the toxicity characteristic HWN was not previously assigned, the HWN will be assigned and counted against AK accuracy.
7. **Toxicity Characteristic VOCs and non-toxic F003 Assignment** can be changed if the TCLP/totals indicate that the concentration of a characteristic waste or non-toxic constituent of an F003 waste is below regulatory levels. The change is not counted against AK accuracy in this paper.
8. **F-listed Solvent Assignment** is confirmed using SS. If an F-listed solvent exceeds the regulatory threshold limit and the solvent has not been identified for the waste stream in the AK record, the F-listed solvent HWN is added. The addition is counted against AK accuracy.

Another metric reported by generators is related to the ongoing characterization of the waste after a waste stream is approved for disposal at WIPP. Container-specific data are required to be transmitted to WIPP prior to the shipment of a container. (See for example HWFP Attachment B3-10c and B-4b(1)(ii)). The WIPP Waste Information System (**WWIS**) verifies that the container belongs to an approved waste stream. This involves ongoing HSGSA and radiography or VE. Cases where there are discrepancies such as a container that belongs in another waste stream or a container that should have additional HWNs applied require resolution by the generator. This metric is useful in determining the accuracy of the information used to assign specific containers to specific waste streams.

9. **Hazardous Waste Assignment** is evaluated on an ongoing basis to determine if containers have hazardous wastes not reported on the Waste Stream Profile Form (**WSPF**), or if a different WMC applies. Changes are included in Metric 2, 3, or 4 as appropriate.

One additional assessment of waste characterization accuracy can be added with regard to prohibited items. Radiography and VE are discussed in the HWFP as methods that are well-suited to identify the presence of certain prohibited items such as liquids in excess of the prohibition and unvented pressurized containers. If generators find prohibited items during radiography or VE, they are expected to take action to mitigate, including removing the prohibited item or taking the container out of the waste stream.

10. **Unexpected Prohibited Items** are identified using radiography or VE. The discovery of an unexpected prohibited item is diagnostic of how well characterization processes are identifying such items.

These ten metrics are discussed in the following pages. All have been included since one or all of the generator sites have reported against these ten items. Even though not all are used to measure AK accuracy for HWFP-required parameters, the metrics provide useful information regarding the efficacy of using AK to meet the HWFP DQOs.

One additional measure of accuracy included in the HWFP is determination of the miscertification rate. This is a measure of radiography quality and not AK accuracy. A miscertification occurs if a container that was determined to meet waste acceptance criteria is subsequently discovered to contain a prohibited item. This determination is made using VE of randomly selected containers of waste that have been certified as meeting the Waste Acceptance Criteria (**WAC**). The number of containers selected each year depends on the historical miscertification rate and the number of containers that will be processed in a year. Permit Attachment B2 describes the statistical method used to determine how many containers must be opened for VE each year. VE used in this manner is a quality control check on the radiography process at a generator site.

Generator sites have procedures for determining AK accuracy and calculating the miscertification rate. The sites have applied the procedures on at least an annual basis. Current reported accuracies are provided in Table 2 for all sites that are shipping waste to WIPP.

Table 2 Overall Acceptable Knowledge Accuracy and Miscertification Rate for Each Site

Site	Hazardous Waste Number Assignment		Waste Stream Assignment	Miscertification Rate	
ANL E-CCP (through July 2003)	99.7% (Note 1)		91.4% (Note 2)	Not determined (Note 3)	
SRS-CCP (March 25, 2003)	99.5% (Note 4)		99.97% (Note 5)	6%	
Hanford (June 18, 2002)	100%		100%	0% (Note 6)	
INEEL (3,100 m ³) (November 27, 2002)	83% (Note 7)		99.4%	S3000	3%
				S5000	0% (Note 6)
LANL (August 27, 2002)	100%		90.23%	6% (7/31/01)	
Rocky Flats (July 24, 2002)	Headspace Gas	99%	99%	0% (Note 6)	
	Solids Sampling	100%			

Note 1: ANL-E reported a lead-lined glove in a container when none was expected based on AK information. D008 was assigned to the waste stream.

Note 2: During repackaging of the first lot of 28 containers, ANL-E concluded that the waste stream should be classified as S5400 instead of S5420. The reassignment was confirmed by all subsequent containers.

Note 3: Waste stream approval was based on 10% VE in lieu of radiography. Annual miscertification rate has not been calculated yet.

Note 4: SRS reports lead in 15 containers and fluorescent tubes in two containers, resulting in reassignments of HWNs due to base materials.

Note 6: Minimum miscertification rate allowed by the HWFP is 1 percent.

Note 7: Based on final 3,100 m³ project numbers.

The following three sections provide a discussion of these AK accuracy results. Section 2.0 provides an analysis and discussion of the assignment of hazardous waste numbers based on sampling and analysis of headspace gas and homogeneous solids. This addresses Accuracy Metrics 4 through 9 in the list of accuracy measures above. The discussion forms the basis for eliminating use of HSGSA and SS for confirming AK information.

Section 3.0 discusses AK accuracy determinations made based on observations of the physical form of the waste. The discussion provides a basis for reducing confirmatory

activity to a statistically selected subset of containers. Section 4.0 discusses miscertification rates, providing a basis for eliminating use of visual VE as a quality control check on radiography. A general discussion of the results is provided in Section 5.0 along with recommendations for new DQOs.

2.0 Hazardous Waste Number Reassignments

An analysis of WSPFs for each waste stream disposed of in WIPP was performed to assess the efficacy of HSGSA as well as SS in confirming Environmental Protection Agency (EPA) HWNs for WAP requirements. Generator sites are required to complete a WSPF for a waste stream once characterization is complete. Characterization is considered to be complete once all required and supplemental AK has been assembled and confirmed by chemical sampling and analysis and waste examination. Following approval of the WSPF, the generator site can begin to ship waste from the waste stream. Each container is subject to confirmation including HSGSA and, in some instances, SS.

The analysis in this section evaluates how many times HWNs were applied in the initial characterization and profile preparation phase of the waste stream as a result of HSGSA or SS. In addition, the analysis looks at how many times confirmation activities performed after the WSPF is approved resulted in identification of additional HWNs for a waste stream or when a container was assigned to another waste stream due after the identification of an additional HWN.

The WWIS was queried to provide a comprehensive listing of waste streams that were approved for shipment to WIPP as of May 2003. These are summarized in Table 3, which includes the waste stream identifier, Summary Category Group (SCG), the number of containers from the waste stream that were shipped to WIPP for disposal, and the number of F-listed HWNs added as a result of HSGSA (Accuracy Metric 4). Changes made by the generator site are discussed in the comment field.

Table 3 Summary of F-listed Hazardous Waste Number Reassignments as the Result of Headspace Gas Sampling and Analysis (Metric 4)

SITE	WASTE STREAM IDENTIFIER	SUMMARY CATEGORY GROUP	NUMBER OF CONTAINERS	HWNs ADDED (NOTE 1)	COMMENTS
ANL-E/CCP	AECHDM	S5000	334 (Note 2)	0	
SRS/CCP	SR-W027-221F-HET A	S5000	2,220 (Note 3)	0	
SRS/CCP	SR-027-FB-PRE86-C	S5000	1,285 (Note 4)	0	
Hanford	RLMPDT.001	S5000	90 (Note 5)	0	Non-mixed
Hanford	RLNPDT.002	S5000	671 (Note 5)	0	Non-mixed
INEEL	INW161.001	S5000	75 (Note 5)	0	
INEEL	INW169.001	S5000	83 (Note 5)	0	Note 6
INEEL	INW198.001	S5000	239 (Note 5)	0	Note 6
INEEL	INW211.001	S5000	1,453 (Note 5)	0	Note 6
INEEL	INW216.001	S3000	6,018 (Note 5)	0	Discrepancy with regard to D022 based on HSGSA -- not F-listed solvent. HWN added, see Table 5.
INEEL	INW218.001	S3000	4,650 (Note 5)	0	Discrepancy with regard to D032 based on HSGSA -- not F-listed solvent. HWN added, see Table 5.
INEEL	INW222.001	S3000	342 (Note 5)	0	Discrepancy with regard to D022

SITE	WASTE STREAM IDENTIFIER	SUMMARY CATEGORY GROUP	NUMBER OF CONTAINERS	HWNS ADDED (NOTE 1)	COMMENTS
					noted by generator -- not F-listed solvent. HWN added, see Table 5.
INEEL	INW243.001	S5000	342 (Note 5)	1	F005 added based on HSGSA. Counts against AK accuracy.
INEEL	INW247.001	S5000	1,575 (Note 5)	0	
INEEL	INW252.001	S5000	13 (Note 5)	4	F001, F002, F003, and F005 added. Count against AK accuracy. D022 noted as a discrepancy. Not F-listed solvent, HWN added, see Table 5.
INEEL	INW276.003	S5000	887 (Note 5)	0	
INEEL	INW276.004	S5000	285 (Note 5)	2	F001, F002, and F005 added based on HSGSA. HWNs added to WSPF. Count against AK accuracy. D008, D029, and D040 noted as a discrepancy. Not F-listed solvent, HWNs added, see Table 5.
INEEL	INW296.001	S5000	389 (Note 5)	0	
LANL	LA-TA-55-19	S5000	256 (Note 7)	0	
RFETS	TRU combustibles and plastics	S5000	2,814 (Note 8)	3	F001, F002, and F005 added based on HSGSA. Count against AK accuracy. 143 containers affected. D022, D028, and D029, noted as a discrepancy. Not F-listed solvent, HWNs added, see Table 5.
RFETS	TRU graphite debris	S5000	29 (500) (Notes 8,9)	0	
RFETS	TRU metal debris	S5000	958 (Note 8)	3	F001, F002, and F005 added based on HSGSA. Count against AK accuracy. 26 containers affected. D022 noted as a discrepancy. Not F-listed solvent, HWNs added, see Table 5.
RFETS	TRU stabilized pyrochemical salts	S3000	15 (373) (Notes 8,9)	0	
RFETS	TRU LECO and crucible inserts	S5000	34 (693) (Notes 8,9)	0	
RFETS	TRU ceramic crucibles	S5000	19 (383) (Notes 8,9)	0	
RFETS	TRU pyrochemical salts	S3000	35 (5,909) (Notes 8,9)	0	
RFETS	TRU filter debris	S5000	333 (Note 8)	1	F005 added based on HSGSA. Count against AK accuracy. One container affected
RFETS	TRM incinerator ash	S3000	73 (5,851) (Notes 8,9)	0	
Total			25,517 (39,021)	10	Waste streams affecting 1202 Containers

Note 1: Number in column indicated the number of HWNs added to the waste stream as the result of HSGSA results in accordance with the HWFP.

Note 2: Number of containers in Lots 1-9 (through July 2003).

Note 3: Number of containers in Lots 1-19 (through March 25, 2003).

Note 4: Number of containers in Lots 1-14 (through March 24, 2002).

Note 5: Number of containers reported in final AK Accuracy Report for 3,100 m³ Project.

Note 6: D009 added and counted against accuracy by INEEL.

Note 7: Based on LANL August 2002 AK Accuracy Assessment.

Note 8: Based on RFETS AK Accuracy Summary dated 7/24/2002.

Note 9: Parenthetical value is the total containers represented by the sampled subset.

Table 4 summarizes the S3000 waste streams that were characterized and provides the

instances when an HWN was added based on SS (Accuracy Metrics 6 and 8).

Table 4 Summary of Toxicity Characteristic Hazardous Waste Number Reassignments as the Result of Solids Sampling and Analysis (Metrics 6 and 8)

SITE	WASTE STREAM IDENTIFIER	SUMMARY CATEGORY GROUP	NUMBER OF CONTAINERS	HWNs ADDED (NOTE 1)		COMMENTS
				6	8	
INEEL	INW216.001	S3000	6,018 (Note 2)	0	0	Discrepancy with regard to D022 based on HSGSA -- not F-listed solvent. HWN added even though solids sampling did not identify D022.
INEEL	INW218.001	S3000	4,650 (Note 2)	0	0	Discrepancy with regard to D022 based on HSGSA -- not F-listed solvent. HWN added even though solids sampling did not identify D022.
INEEL	INW222.001	S3000	342 (Note 2)	0	0	Discrepancy with regard to D022 noted by generator -- not F-listed solvent. HWN added even though solids sampling did not identify D022.
RFETS	RF005.01	S3000	13 (574) (Note 3)	0	0	
RFETS	RF009.01	S3000	49 (6,207) (Note 3)	0	0	
RFETS	RF118.01	S3000	26 (6,801) (Note 3)	0	0	
RFETS	RF128.01	S3000	744 (Note 4)	2	0	Discrepancy with regard to D008 and D011 noted by Solids Sampling. HWNs added.
Total			11,842 (25,336)	1 Waste stream affecting 744 Containers		

Note 1: Number in column indicated the number of HWNs added to the waste stream as the result of SS in accordance with the HWFP.

Note 2: Number of containers reported in final AK Accuracy Report for 3,100 m³ Project.

Note 3: Number of container sampled as reported in the July 24, AK Accuracy Report. Parenthetical number is the number of containers in the WWIS from this waste stream as of May 23, 2003.

Note 4: This discrepancy was identified by RFETS on the waste stream profile form subsequent to the most recent AK Accuracy Report and is included here since it represents HWNs added based on SS.

There are other items that generator sites report as part of their AK accuracy reports. For example, INEEL assigned several toxicity characteristic HWNs to debris waste based on the results of HSGSA as summarized in Table 5. Clearly finding chemicals such as chloroform (D022) in the headspace in concentrations above the established regulatory threshold limits when the AK information does not indicate such presence represents a discrepancy. However, in dealing with this situation, the permit is specific. The permit only addresses confirmation of the assignment of F-listed HWNs using HSGSA in Attachment B4-3d. With regard to the "concentration of applicable toxicity characteristic solvents", the HWFP allows the removal of such HWNs based on HSGSA, if the concentration in the headspace gas would render the waste non toxic. The HWFP does not specifically require the addition of toxicity characteristic HWNs based on HSGSA. Likewise in Attachment B4-3d in the discussion of using SS and HSGSA together, the permit uses "i.e." instead of "e.g." in the parenthetical statement which defines a discrepancy as the situation where the compound appears in the solids sample and not in the headspace gas sample. This text also reinforces that toxicity characteristic codes need not be assigned based solely on HSGSA. This notwithstanding, one site has reported the assignment of a toxicity HWN based on HSGSA results alone. That is, the solids sampling did not support the assignment. This is a conservative application of HWNs by the generator site. This discrepancy is reported in this paper because it affects a large number of containers. However, it is counted against the AK accuracy only in the case of debris waste since for debris waste there is no corroborating sampling and analysis information indicating that the chemical is not present in the waste.

During ongoing waste analysis, RFETS tracks and reports the number of containers that have additional HWNs applied to them based on HSGSA (Metric 9). These are shown in Table 6 and they are accounted for in Table 3 for the purpose of AK accuracy determination because they involve F-listed solvents.

Table 5 Instances Where INEEL Added Toxicity Characteristic HWNs to the Waste Stream Profile Form (not from AK Information)

SITE	WASTE STREAM IDENTIFIER	SUMMARY CATEGORY GROUP	NUMBER OF CONTAINERS (NOTE 1)	TC HWNS ASSIGNED	COMMENTS
INEEL	INW169.001	S5000	83	D009	HWN assigned to WSPF. Note that the INEEL AK Accuracy report is not specific regarding the method by which the D009 code was identified.
INEEL	INW198.001	S5000	239	D009	HWN assigned to WSPF. Note that the INEEL AK Accuracy report is not specific regarding the method by which the D009 code was identified.
INEEL	INW211.001	S5000	1,453	D009	HWN assigned to WSPF. Note that the INEEL AK Accuracy report is not specific regarding the method by which the D009 code was identified.
INEEL	INW216.001	S3000	6,018	D022	HWN assigned to WSPF. Note that the WSPF indicates that D022 was assigned based on HSGSA and solids sampling did not detect D022.
INEEL	INW218.001	S3000	4,650	D032	HWN assigned to WSPF. Solids sampling did not support the addition of this code. Note 2
INEEL	INW222.001	S3000	342	D022	HWN assigned to WSPF. Note that the WSPF indicates that D022 was assigned based on HSGSA and solids sampling did not detect D022.
INEEL	INW252.001	S5000	13	D022	HWN assigned to WSPF.
INEEL	INW276.004	S5000	285	D008, D029, D040	HWN assigned to WSPF.
TOTAL			13,083 (2,073)		2,073 containers counted against AK accuracy

Note 1: Number of containers reported in final AK Accuracy Report for 3,100 m³ Project.

Note 2: The WSPF for this waste stream indicates that D032 is indicated in 1997-1998 solids sampling results. It was not detected above the regulatory threshold limit in the current sampling. The code was added as a conservative measure. Showing it as an AK discrepancy appears to be an error by INEEL since the WSPF AK Summary indicated the possible presence of the compound based on previous analytical data.

Table 6 Instances Where RFETS Assigned HWNs to Containers Based on the Results of Headspace Gas Sampling and Analysis (Metric 9)

SITE	WASTE STREAM	NUMBER OF CONTAINERS	NUMBER OF CONTAINERS WITH VOCs ABOVE PRQL	HWNS ASSIGNED
RFETS	TRU combustibles and plastics	2,814	143	D022, D028, D029, F001, F002, F005
RFETS	TRU graphite debris	29 (500) (Note 1)	0	
RFETS	TRU metal debris	958	26	D022, F001, F002, F005
RFETS	TRU stabilized pyrochemical salts	15 (373) (Note 1)	0	
RFETS	TRU LECO and crucible inserts	34 (693) (Note 1)	0	
RFETS	TRU ceramic crucibles	19 (383) (Note 1)	0	
RFETS	TRU pyrochemical salts	35 (5,909) (Note 1)	0	
RFETS	TRU filter debris	333	1	F005

SITE	WASTE STREAM	NUMBER OF CONTAINERS	NUMBER OF CONTAINERS WITH VOCs ABOVE PRQL	HWNS ASSIGNED
RFETS	TRM Incinerator ash	73 (5,851) (Note 1)	0	
TOTAL		4,310 (17,814)	170	

Note 1: These waste streams consist of waste that was produced through a thermal process and that underwent statistical sampling. The number shown is the number of samples taken. The number in parentheses is the number of containers in the waste stream.

Finally, other changes were made to add or delete HWNs on the WSPF after characterization by INEEL. These changes were based on subsequent AK information developed by INEEL. These are provided in Table 7. INEEL did not include these changes in their accuracy calculations.

Table 7 Other Hazardous Waste Number Assignments Made by INEEL Prior to Completing the Waste Stream Profile Form Based on Subsequent AK Information.

SITE	WASTE STREAM IDENTIFIER	SUMMARY CATEGORY GROUP	NUMBER OF CONTAINERS (NOTE 1)	HWNS ASSIGNED	COMMENTS
INEEL	INW161.001	S5000	75	F006 added F007 added F009 added	HWN change as the result of subsequent AK. INEEL did not count against AK accuracy
INEEL	INW169.001	S5000	83	D001 deleted D002 deleted	HWN change as the result of subsequent AK. INEEL did not count against AK accuracy
INEEL	INW198.001	S5000	239	D001 deleted D002 deleted	HWN change as the result of subsequent AK. INEEL did not count against AK accuracy
INEEL	INW211.001	S5000	1,453	D022 added F003 deleted	HWN change as the result of subsequent AK. INEEL did not count against AK accuracy
INEEL	INW216.001	S3000	6,018	D002 deleted F003 deleted	HWN change as the result of subsequent AK. INEEL did not count against AK accuracy
INEEL	INW218.001	S3000	4,650	D006 added D008 added D009 added D011 added D002 deleted F003 deleted	HWN change as the result of subsequent AK. INEEL did not count against AK accuracy
INEEL	INW222.001	S3000	342	F006 added F007 added F009 added D002 deleted	HWN change as the result of subsequent AK. INEEL did not count against AK accuracy
INEEL	INW243.001	S5000	342	D022 added F001 added F002 added D001 deleted D002 deleted	HWN change as the result of subsequent AK. INEEL did not count against AK accuracy
INEEL	INW247.001	S5000	1,575	D008 added D002 deleted	HWN change as the result of subsequent AK. INEEL did not count against AK accuracy
INEEL	INW252.001	S5000	13	F006 added F007 added F009 added D003 deleted	HWN change as the result of subsequent AK. INEEL did not count against AK accuracy
INEEL	INW296.001	S5000	389	D028 added D001 deleted	HWN change as the result of subsequent AK. INEEL did not count against AK accuracy

Note 1: Number of containers reported in final AK Accuracy Report for 3,100 m³ Project.

To date, there are ten waste streams where HSGSA resulted in the assignment of a new

F-listed HWN after it was characterized based on AK information. This affected 1,202 containers of waste. All of the HWNs added were allowed by the HWFP. **The addition of the HWNs did not change the sampling and analysis or the way in which the waste stream was handled.**

In the case of the homogeneous solids waste stream, there was one instance when SS resulted in the addition of two characteristic HWNs, affecting 744 containers. In this case, the waste stream was already considered to be a mixed waste stream, containing both listed and characteristic waste. **Once again, the confirmation did not change the status of the waste stream, nor did it result in additional handling or management requirements.**

In other instances, INEEL added toxicity characteristic HWNs to debris waste streams based on HSGSA. This affected five waste streams containing 2,073 containers. **The addition of the HWNs did not change the status of the waste stream, nor did it result in additional handling or management requirements.**

Overall, 10.3 percent of the waste containers had new HWNs assigned to them through the confirmatory process (see Table 8). In addition, other assignments have been conservatively made to numerous waste streams and individual containers. In no case did the assignments change the manner in which the waste was managed nor did it affect the disposal process. **There were no recorded instances where the results of HSGSA or SS resulted in the removal of a container from the generator sites' transuranic (TRU) waste inventory because it was determined to be unsuitable for disposal in WIPP.**

The following conclusions can be stated:

- No unauthorized HWNs were identified.
- No prohibited waste was identified.
- The AK information for HWNs is about 90 percent accurate.
- None of the constituents found as the result of HSGSA or SS rendered the container or waste stream unsafe for shipment to or handling, storage or disposal at WIPP.

Table 8 Summary of Number of Containers Disposed in WIPP That Were Assigned New Hazardous Waste Numbers

Total Containers Considered	39,021
HWNs added based upon HSGSA	3,274
HWNs added based upon SS	744
Total Number Containers HWNs added by HSGSA /SS	4,018
HWN Accuracy	89.7%

3.0 Radiography and Visual Examination

Generator sites report AK accuracy using radiography or VE from two aspects. First, the number of containers assigned a new WMC are reported as a percentage of the total number of containers examined (**Metrics 1, 2, and 10**). Second, sites report the number of new HWNs assigned to a container and a waste stream based on the identification of "base materials" using radiography or VE (e.g., the identification of a leaded apron using radiography would result in the addition of the D008 HWN) (**Metric 3**).

Table 9 summarizes the number of containers assigned a different WMC. These are provided by WMC for the various generator sites.

Table 9 Waste Matrix Code Assignments Using Radiography or Visual Examination (Metrics 1 and 2)

SITE	WASTE MATRIX CODE	NUMBER OF CONTAINERS EXAMINED	NUMBER OF CONTAINERS REASSIGNED	DATE OF AK ACCURACY REPORT
ANL-E/CCP	S5400 (Visual Examination in lieu of radiography)	56	6 (Note 1)	Number of containers in Lots 1-9 (through July 2003).
ANL-E/CCP	S5400 (Radiography)	280	0	Number of containers in Lots 1-9 (through July 2003).
SRS/CCP	S5420	1,285	251 (Note 2)	Number of containers in Lots 1-14 (through March 24, 2002).
SRS/CCP	S5440	2,220	1	Number of containers in Lots 1-19 (through March 25, 2003)
Hanford	Debris	19	0	June 18, 2002 AK Accuracy Report.
INEEL	All IDCs	25,531	159	Number of containers reported in final AK Accuracy Report for 3,100 m ³ Project.
LANL	SCG S5000 (Radiography)	2,088	187	AK Accuracy Report dated 8/27/02
LANL	SCG S5000 (Visual Examination)	85	6	
RFETS	S3111	6	0	July 24, 2002 AK Accuracy Report, Table 2.2-1
RFETS	S3114	1	0	
RFETS	S3119	14	0	
RFETS	S3121	23	0	
RFETS	S3141	2,617	0	
RFETS	S3190	110	0	
RFETS	S3211	2	0	
RFETS	S3229	1	0	
RFETS	S3290	3	0	
RFETS	S5111	1,475	72	
RFETS	S5112	75	2	
RFETS	S5119	5	0	

SITE	WASTE MATRIX CODE	NUMBER OF CONTAINERS EXAMINED	NUMBER OF CONTAINERS REASSIGNED	DATE OF AK ACCURACY REPORT
RFETS	S5122	370	0	
RFETS	S5123	1,102	0	
RFETS	S5126	540	1	
RFETS	S5129	51	0	
RFETS	S5311	365	0	
RFETS	S5313	6	0	
RFETS	S5319	1	0	
RFETS	S5390	3,919	14	
RFETS	S5410	567	7	
RFETS	S5420	8	0	
RFETS	S5490	169	0	
RFETS	Residues (VE)	4,219	10	
TOTAL		47, 213	716	July 24, 2002 AK Accuracy Report, Table 2.5-1

Note 1: Six containers in the first lot could not be confirmed as S5420. Reevaluation of the AK resulted in the assignment of the entire waste stream to a different (more general) WMC. Subsequent examination supported the new WMC assignment.

Table 10 summarizes the number of times a generator site changed the toxicity characteristic HWN assignment associated with a container, based on results of radiography or VE (Metric 3). In some cases, the generator noted the base material that may have a toxicity characteristic HWN assigned to it (e.g., a leaded apron). In such instances, the HWN assignment is counted against AK accuracy as required by Metric 3. At RFETS, when radiography resulted in the assignment of a container to a new WMC, the HWN assignment may also have changed to be consistent with the new WMC. In such cases, the assignment of the new WMC is counted against AK accuracy (and is included in Table 10) however, the change in HWN is not counted against AK accuracy since the new HWNs are changed to be consistent with the new WMC and its associated HWN suite.

Table 10 Hazardous Waste Number Changes Made as the Result of Radiography or Visual Examination (Metric 3)

SITE	WASTE STREAM DESCRIPTION	NUMBER OF CONTAINERS EXAMINED	NUMBER OF CONTAINERS WITH CHANGED HWNs (NOTE 1)	SOURCE
ANL-E/CCP	S5400	336	1 (1)	Number of containers in Lots 1-9 (through July 2003).
SRS/CCP	SR-W027-FB-Pre86-C	1,285	0	Number of containers in Lots 1-14 (through March 24, 2002).
SRS/CCP	SR-W027-221F-Het-A	2,220	17 (17)	Number of containers in Lots 1-19 (through March 25, 2003)
HANFORD	NONE	1,152	0	June 18, 2002 AK Accuracy Report.
INEEL	NONE	25,531	0	Number of containers reported in final AK Accuracy Report for 3,100 m ³ Project.
LANL	TA-03-14	1	0	AK Accuracy Report dated 8/27/02 Table 3
LANL	TA-55-19	1,084	8 (8)	
LANL	TA-55-20	9	0	
LANL	TA-55-21	464	6 (6)	
LANL	TA-55-22	32	0	
LANL	TA-55-23	36	1 (1)	
LANL	TA-55-24	6	0	
LANL	TA-55-28	12	0	
LANL	TA-55-30	309	0	
LANL	TA-55-31	47	0	
LANL	TA-55-43	52	0	
LANL	TA-55-44	26	2 (2)	

SITE	WASTE STREAM DESCRIPTION	NUMBER OF CONTAINERS EXAMINED	NUMBER OF CONTAINERS WITH CHANGED HWNs (NOTE 1)	SOURCE
LANL	TA-55-46	9	0	July 24, 2002 AK Accuracy Report, Tables 2.2-1 and 2.2-2
LANL	TA-55-47	1	0	
RFETS	S3111	6	0	
RFETS	S3114	1	0	
RFETS	S3119	14	0	
RFETS	S3121	23	0	
RFETS	S3141	2,617	0	
RFETS	S3190	110	0	
RFETS	S3211	2	0	
RFETS	S3229	1	0	
RFETS	S3290	3	0	
RFETS	S5111	1,475	3 (1) (Note 2)	
RFETS	S5112	75	6 (6)	
RFETS	S5119	5	0	
RFETS	S5122	370	5 (4) (Note 3)	
RFETS	S5123	1,102	0	
RFETS	S5126	540	0	
RFETS	S5129	51	0	
RFETS	S5311	365	0	
RFETS	S5313	6	0	
RFETS	S5319	1	0	
RFETS	S5390	3,919	50 (17) (Note 4)	
RFETS	S5410	567	4 (2) (Note 5)	
RFETS	S5420	8	0	
RFETS	S5490	169	0	
TOTAL		44, 402	103 (65)	

Note 1: Number in parentheses indicates number of changes that count against AK accuracy.

Note 2: Includes two containers of metals that were reassigned to combustible. New codes added due to combustible AK information. One container of metal found not to have liquid, D003 removed.

Note 3: One container of leaded glass found to be glass. Codes changed based on AK information for glass.

Note 4: 32 containers of wet combustibles found to be plastics. HWNs reassigned based on plastics AK information.

Note 5: One container of plastics found by RTR to be firebrick, HWNs reassigned based on AK information for firebrick.

Note 5: Two containers of processes HEPA filter media found by RTR to be Ful-Flo filters, HWNs reassigned based on AK information for Ful-Flo filters.

Although not specifically called out by the HWFP as an AK accuracy measure, several sites have reported the discovery of prohibited items in narrative associated with their AK accuracy reports. These are summarized in Table 11. There are three types of data included in Table 11. First, some sites indicate that a prohibited item was found during radiography when it was not expected. Second, one site (ANL-E/CCP) indicates that AK information on some waste streams includes the possibility that a prohibited item may be found. Most sites do not include this type of occurrence of a prohibited item in a container undergoing radiography or VE in their AK accuracy reports. Instead they remove the waste container from the waste inventory being considered for shipment until the item is remediated. Neither of these types of occurrences of prohibited items are considered to be miscertifications since the prohibited item was not found in a certified container of waste. The third type of data included in Table 11 is reported discoveries of prohibited items during VE as a quality control check (QC) on radiography. These containers are considered to be "miscertified."

Table 11 Summary of Reported Instances When Prohibited Items Were Found During Radiography or Visual Examination (includes VE as a QC Check on Radiography)

SITE	CONTAINERS RADIOGRAPHED	CONTAINERS VISUALLY EXAMINED	CONTAINERS WITH PROHIBITED ITEMS	SOURCE
ANL-E/CCP	334	92	13 (Note 1)	Number of containers in Lots 1-9 (through July 2003).
SRS/CCP	3,505	50	3	Number of containers through March 25, 2003.
HANFORD	761	15	0	Hanford Miscertification Rate Calculation for FY 2003 dated 3/6/03. Number of containers in WWIS as of May 23, 2003.
INEEL	25, 531	144	4	Note 2
LANL	2,088	85	3	AK Accuracy Report dated 8/27/02 and LANL miscertification calculation dated 8/24/00.
RFETS	11,430	149	6 (Note 3)	July 24, 2002 AK Accuracy Report
TOTAL	43, 649	535	29	

Note 1: These 13 items were expected based on the AK information for the waste stream.

Note 2: The final closeout report for the 3,100 m³ Project does not calculate a final miscertification rate. The number of containers is all the containers radiographed by the project. The number of visually examined containers is those known to have been examined as of June 2001 and the prohibited items are those reported as of that time. It is anticipated that another 60 containers were examined in 2002.

Note 3: These 6 items were unexpected in the waste streams undergoing radiography.

The information in Table 11 is included for completeness (i.e., the data are reported in the generator site AK accuracy reports). This information must be used carefully since many sites do not report the number of containers that are rejected by the radiography or VE in lieu of radiography processes.

Cumulatively, generator sites have radiographed or visually inspected more than 40,000 containers of waste. **The waste examination has shown that the AK information is very accurate, with a composite AK accuracy of 98.5 percent with regard to WMC or waste stream reassignments (Table 9) and with HWN reassignment based on the observation of base materials only occurring 0.15 percent of the time (Table 10). In addition, less than 0.6 percent of the containers examined had unexpected prohibited items reported.**

Based on these observations, the following can be stated with regard to AK accuracy:

- AK records have been extremely reliable throughout the complex, with regard to the segregation into waste streams.
- AK records have been extremely reliable throughout the complex, with regard to the assignment of waste matrix codes.
- In only a few instances were new HWNs added due to observation of base materials that could exhibit the toxicity characteristic.
- Only six containers were identified through radiography as ineligible for shipment to WIPP because of a new HWN assignment. All are at RFETS and are associated with identification of free liquids in the waste. The liquids were characterized as prohibited using AK.
- The number of unexpected prohibited items in the waste is insignificant;

generally involving presence of unvented containers or liquids in excess of the HWFP limits.

4.0 Miscertification Rate

Although not a measure of AK accuracy, generator sites are required to calculate the miscertification rate associated with the use of radiography. An initial rate of 11 percent is used until sufficient containers have been processed to determine a site-specific rate. The minimum number of containers is 50. Most sites have established site-specific miscertification rates. Some have established rates for both Summary Category Group S5000 debris and Summary Category Group S3000 Homogeneous Solids. Table 12 provides a summary of historical and current miscertification rates for various sites that are shipping waste to WIPP.

Table 12 Annual Miscertification Rates for Each Generator Site Shipping Waste to WIPP (Metric 10)

SITE	SUMMARY CATEGORY GROUP	TOTAL NUMBER OF CONTAINERS			MISCERTIFICATION RATE FOR EACH CALENDAR YEAR (Notes 1 and 2)			
		RADIO-GRAPHED	VISUALLY EXAMINED	MISCERTIFIED	2000	2001	2002	2003
ANL-E/CCP	S5000	280	56	0			11	
SRS/CCP	S5000	3,505		3		11	6	
HANFORD	S5000	1,243		0	11		0	0
INEEL	S3000	10,489		2		5	3	
	S5000	4,933		2	11	3	0	
LANL	S5000	2,088	85	3	11	6		
RFETS	S3000	2,767	16	0		0	0	
	S5000	8,663	133	0	11	0	0	0

Note 1: The miscertification rate in the first year is 11% until a site-specific rate is established.

Note 2: The minimum rate allowed by the HWFP is 1%; therefore, actual rates of 0% are implemented at minimum.

Generally, miscertification rates are low and do not reveal any systematic or pervasive issues with the quality of radiography being performed at the generator sites. This is in part because the radiography process includes numerous other quality controls to ensure reliable application of the process. Because of these other controls (e.g., training, replicate scans) the practice of intrusively examining containers of waste as a QC check on radiography should be eliminated.

5.0 Discussion

Since the outset of the WIPP waste characterization program, both the Environmental Protection Agency and the New Mexico Environment Department (NMED) have expressed an interest in the reliability of information used by DOE to meet the waste characterization requirements. This interest led both regulatory agencies to require that waste characterization information be confirmed as a means of assuring that information collected was adequate. Indications for this requirement can be found in many historical documents associated with development of the WAP and the issuance of the HWFP as follows:

August 1990 - DOE publishes the Program Plan for the Pretest Characterization of WIPP Experimental Waste, DRAFT Revision 6.0, DOE/WIPP 89-025 describing proposed TRU waste characterization activities to support the bin-scale tests at WIPP (to be performed under the No-Migration Variance). This document discusses

various characterization activities including HSGSA and SS, as well as "verification" of process knowledge.

March 1, 1991 - DOE sends a letter to New Mexico Environmental Improvement Division (**NMEID**) inviting the agency to a meeting with EPA to discuss waste characterization issues. The letter included Department of Energy Strategy Document for WIPP, and said "...*This strategy document outlines how the Department of Energy intends to comply with waste analysis requirements pursuant to the RCRA...*". Among other things, the document discusses how DOE would use HSG and AK to verify RCRA-listed waste.

March 7, 1991 - DOE holds a joint meeting with EPA and NMEID to discuss the RCRA compliance strategy for WIPP. Summary notes from this meeting indicate that "...*NMEID, in general, seemed to feel that process knowledge may not be adequate to verify the waste and would like more analysis done... EPA seemed satisfied with headspace sampling as an adequate verification tool, along with process knowledge, RTR and visual examination for easily characterized waste...*"

October 10, 1991 - Representatives of DOE and NMED meet to discuss WIPP's waste analysis plan and waste characterization requirements. Summary notes from the meeting state "...[NMED] *emphasized that the waste characterization program is key to the NMED review of the entire permit application...[NMED] also indicated that in cases where DOE is relying heavily on knowledge of materials and processes, we must provide information demonstrating the reliability of this knowledge...[NMED] also indicated that DOE commitments regarding sampling frequencies are to define the 'representativeness' of DOE sampling and analyses plans... The Waste Analysis Plan is the document that the NMED will review for the completeness of all waste characterization requirements under RCRA...*"

September 29, 1992 - NMED sends a letter to DOE clarifying statements made in the August 25, 1992 Notice of Deficiency. This letter includes an extensive discussion of NMED expectations regarding process knowledge and verification.

October 26, 1995 - Representatives of WIPP and NMED, and their respective contractors, met in Santa Fe to discuss NMED comments on the WAP included in the latest revision of WIPP's RCRA permit application. Summary notes from the meeting say "...*The NMED expressed disappointment at what they considered many deficiencies in Chapter C, the Waste Analysis Plan (WAP). It had been structured completely different from Revision 3 which described the Test Program. They stated that there is a lack of specific detail in many areas and the use of 'acceptable knowledge' needs to be fully described...The NMED wants to see the entire process laid out clearly for the DOE's application of 'acceptable knowledge' ...Demonstration of acceptable knowledge has to be a process that can be evaluated. Clarification is needed to explain how information is acquired at the generator sites to make the initial waste classifications and assign EPA hazardous waste codes...Verification of acceptable knowledge is also a significant issue...*"

The requirement for one hundred (100) percent headspace gas sampling is necessary because it is a key confirmatory analysis in the acceptable knowledge process and the only chemical analytical method used for debris waste characterization [NMED Direct Written Testimony Regarding Regulatory

In summary, headspace gas compounds, including TICs [Tentatively Identified Compounds], contained in the hazardous waste disposed at WIPP must be identified and quantified to ensure that (1) the accuracy of hazardous waste codes assigned to a waste stream; (2) the proper characterization of waste; and (3) the protection of human health and the environment from releases of hazardous waste. To this end, the TIC permit condition, based on SW-846 Methods and the Appendix VIII list, is both reasonable and necessary. [NMED Direct Written Testimony Regarding Regulatory Process and Imposed Conditions, IV. Imposed Conditions, Module II, Tentatively Identified Compounds, page 7 of 7]

The data reported to date from generator sites have indicated that the concerns regarding waste characterization accuracy generally and AK accuracy specifically, are, for the most part, unfounded.

Clearly, AK information is not perfect; there are a finite number of errors detected in the course of waste characterization. Specifically, of nearly 40,000 containers that have been fully characterized, hazardous waste numbers were changed 10 percent of the time. Likewise, out of nearly 47,000 containers subjected to radiography or VE in lieu of radiography, the WMC or waste stream assignment was changed 1.5 percent of the time.

With more than 40,000 containers disposed at WIPP, the use of AK has proven to be effective for characterizing waste. Verification of information collected through the AK process has resulted in generally high AK accuracies. The DQOs established by the HWFP are being met with a high degree of confidence.

The workability of this new approach depends on two factors. First, the compilation of AK information must be robust and complete. Generator sites can no longer accept waste into the WIPP characterization program if AK information indicates the possibility of prohibited items similar to the waste stream characterized from ANL-E. In this case, the stream would have to be pre-screened, using radiography or VE, for adequate assurance that no prohibited items exist. Likewise, if HWNs are unknown, effort will be necessary to make reasonable assignments to assure there is no compatibility issue associated with the waste. Second, success depends on the construction of an adequate waste examination sampling plan. This examination of the data collected to date indicates that a statistical sampling approach could be used to identify the number of containers that should be radiographed or subjected to VE to confirm the waste stream characterization results with a high degree of confidence.

In conclusion, the high accuracies dispel the belief that generator site AK requires confirmation through intrusive HSGSA and SS in order to safely manage the waste. In fact, there are no reported instances of changes as the result of HSGSA and SS that required different handling or disposal provisions. In that sense, HSGSA and SS are redundant to AK information which has been proven to provide the information necessary to ensure safe/protective management of the waste. It is on this basis that these unnecessary methods cannot be justified as required elements of WIPP's HWFP WAP. Certainly, it remains important to be diligent in the AK process and to carefully confirm the AK record but this can be effectively done using radiography or visual examination of a representative subpopulation of the waste. Waste examination, either

visually or through radiography, can directly confirm the physical properties of the waste, the absence of most prohibited items and, therefore, indirectly confirm the chemical/hazardous properties of the waste.

DRAFT

D R A F T

**Statutory, Regulatory and Guidance Justification
for Changing Mixed Waste Analysis
Requirements at the Waste Isolation Pilot Plant**

Prepared by the U.S. Department of Energy, Carlsbad Field Office
Technical Assistance Contractor (CTAC)
September 4, 2003

Statutory, Regulatory, and Guidance Justification for Changing Mixed Waste Analysis Requirements at the Waste Isolation Pilot Plant

Executive Summary

This paper examined the statutes, regulations, and guidance applicable to mixed waste analysis at the Waste Isolation Pilot Plant (WIPP) that were established under the Resource Conservation and Recovery Act (RCRA), the Atomic Energy Act (AEA), and the Land Withdrawal Act (LWA). It also describes waste characterization and waste analysis plan requirements for generators and Treatment, Storage, and Disposal Facilities (TSDFs) that generate and/or receive mixed waste. Differences in the laws and regulations that were intended for hazardous-only wastes and how they apply to performance based miscellaneous units, such as the WIPP managing mixed waste, are discussed. Relief from these differences is captured in Environmental Protection Agency (EPA) and Nuclear Regulatory Commission (NRC) joint guidance that emphasizes the use of process knowledge alone, whenever possible, to perform a hazardous waste determination. The joint guidance emphasizes the use of process knowledge to avoid unnecessary exposures to radioactivity.

Critical analysis presented in this paper demonstrate that no statutory or regulatory roadblocks preclude WIPP from modifying the Hazardous Waste Facility Permit (HWFP) to allow the exclusive use of waste knowledge (coupled with examination of a representative subpopulation of the waste stream) to satisfy requirements for waste analysis plans. Federal guidance, available in the absence of codified characterization requirements for mixed waste, further supports this position. The *Joint NRC/EPA Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste*, 62 FR 62081, November 1997, emphasizes of the use of process knowledge alone, whenever possible, to perform waste characterization.

There is no statutory or regulatory basis for requiring the examination, sampling and analysis of 100 percent of the containers in every waste stream. The EPA does require the verification of characterization information by the examination or analysis of a representative sample, which may be satisfied by radiographic examination of a representative subpopulation of containers. The EPA and NRC recommend using available characterization methods that will provide the necessary information and minimize workers' exposure to ionizing radiation.

Purpose of this Paper

This paper evaluates statutes, regulations, and guidance to determine whether the WIPP HWFP Waste Analysis Plan (WAP) should be modified to rely on the exclusive use of "acceptable knowledge" (AK), or waste knowledge, for characterizing transuranic (TRU) and TRU mixed waste and to minimize verification activities.

Brief Answer

The EPA clarified in 40 CFR 264.13(a) and the *Joint NRC/EPA Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste*, 62 FR 62081, November 1997 (joint NRC/EPA guidance) that the use of waste knowledge, or AK, i.e. process knowledge, chemical abstracts and generator-developed information, can provide sufficient information to satisfy the requirements of a waste analysis plan. This information could also be used to ensure that a waste disposal facility managed waste in a manner that is protective of human health and the environment. The joint NRC/EPA guidance also considered the reliance on waste knowledge to be particularly appropriate for mixed waste.

The statutes, regulations, and guidance, as cited in this paper, clearly permit the exclusive use of waste knowledge to satisfy the requirements of Title 40 Code of Federal Regulations (CFR) §264.13(a). The joint NRC/EPA guidance indicates that AK is the most appropriate method for characterizing mixed waste. Verification that waste conforms to characterization data, satisfying 40 CFR §264.13(b) requirements, should

also use the least intrusive method possible to minimize worker exposure to ionizing radiation. The WIPP HWFP WAP should be modified to implement these methods, which are equally effective as the current WAP requirements. These methods are also equally protective of human health and the environment, and are more protective of workers' health.

Discussion

The WIPP HWFP WAP has some unique considerations. First, because WIPP is a deep geologic repository, it is permitted as a "miscellaneous unit" pursuant to 40 CFR Subpart X. Subpart X miscellaneous units must operate in a manner that will ensure protection of public health and the environment. The WIPP demonstrates compliance with the environmental performance standards through compliant container and repository management practices and VOC air monitoring programs. As such, the WIPP HWFP WAP should also be written with the goal of supporting these facility operations and demonstrating compliance with VOC air emission limits. Second, the waste sent to WIPP is in final form and is destined for disposal only. No treatment is carried out at the facility and storage is only incidental to disposal. Therefore, concerns related to mixing of wastes in impoundments, tanks or piles are not applicable at WIPP. Third, the waste delivered to WIPP originates within the DOE complex and is typically well pedigreed and subject to strict quality assurance requirements. The documentation upon which hazardous waste determinations are made complies with rigorous quality assurance programs that are audited by the Department of Energy (DOE) Carlsbad Field Office (CBFO), the EPA, the New Mexico Environment Department (NMED), and other states.

The Statutory and Regulatory Bases

The following paragraphs lay the legislative foundation that has led to the current pending legislative action. In summary, the Atomic Energy Act of 1954 was enacted to establish control and safe management of radioactive materials. This Act led to the Energy Reorganization Act of 1974 that assigned the responsibility for defense-related nuclear materials and waste to the Department of Energy (DOE). While DOE was

searching for a solution to the nation's transuranic waste problem, Congress enacted the Resource Conservation and Recovery Act in 1976 to control the disposal of hazardous wastes and assigned responsibility to the EPA. Congress then enacted the Land Withdrawal Act in 1994 to reserve land in southeast New Mexico for the disposal of TRU waste in a deep geologic repository. Congress also exempted transuranic waste from RCRA treatment standards. Yet, there are no codified regulations to specifically address the characterization requirements necessary to dispose of TRU mixed wastes. Facilities are left simultaneously trying to comply with the requirements of RCRA while mitigating the additional hazards of radioactivity.

The Atomic Energy Act of 1954, as amended, is the fundamental U.S. law governing both the civilian and the military uses of nuclear materials. The declared intent of the Act, as stated in Title 42 United States Code (USC) Section 2011 is: "Atomic Energy is capable of application for peaceful as well as military purposes. It is therefore declared to be the policy of the United States that, a) the development, use, and control of atomic energy shall be directed so as to make the maximum contribution to the general welfare, subject at all times to the paramount objective of making the maximum contribution to the common defense and security..." Section 2013 states, "It is the purpose of this Act to effectuate the policies set forth above by providing for, ...c) a program for Government control of the possession, use, and production of atomic energy and special nuclear material..." It is important to understand that Congress enacted this legislation to ensure the control and safe management of nuclear materials in the U.S. and that legislation led to the Energy Reorganization Act. This Act of 1974 established the Nuclear Regulatory Commission and assigned to one agency, now the Department of Energy, responsibility for the development and production of nuclear weapons, promotion of nuclear power, and other energy-related work. The legislation was enacted by Congress and required the DOE to safely manage its own nuclear materials and waste generated as a result of defense-related activities. The DOE subsequently began efforts to identify a suitable disposal solution to the nation's defense-related TRU waste problem, which ultimately became the WIPP.

In 1994, Congress enacted and in 1996 amended the WIPP Land Withdrawal Act to help accomplish the nation's goals related to safe disposal of defense-related TRU waste. Section 3 of the WIPP Land Withdrawal Act, *Land Withdrawal and Reservation for WIPP*, set aside the WIPP property. Section 5, *Definitions*, stated, "As used in this Act, 'Waste Isolation Pilot Plant' means the research and development facility authorized under section 213 of the Department of Energy National Security and Military Applications of Nuclear Energy Authorization Act of 1980 (Public Law 96-164, 93 Stat. 1265) to demonstrate the safe disposal of radioactive waste materials generated by defense programs." Section 9, *Compliance with Environmental Laws and Regulations*, specifically exempted WIPP from required treatment standards under 40 CFR Part 268, *Land Disposal Restrictions* (LDRs). Section 9 provided, "With respect to transuranic mixed waste designated by the Secretary for disposal at WIPP, such waste is exempt from treatment standards promulgated pursuant to section 3004(m) of the Solid Waste Disposal Act (42 U.S.C. 6924(m)) and shall not be subject to the land disposal prohibitions in section 3004(d), (e), (f), and (g) of the Solid Waste Disposal Act." Congress exempted waste destined for the WIPP from the LDRs because they believed that the disposal and repository performance requirements imposed by 40 CFR 191 were stringent enough to accommodate both the radioactive and hazardous waste hazards and, therefore, duplicative regulations were not required.

Prior to the assignment of responsibility for defense-related nuclear waste to the Department of Energy, the U.S. Congress enacted the Solid Waste Act in 1965, largely as an afterthought to a bill dealing with air quality issues. [P.L. 89-272]. The Resource Conservation and Recovery Act of 1976 (RCRA) amended the Solid Waste Act to establish a "cradle to grave" hazardous waste management system to ensure that hazardous waste would be safely treated, stored and disposed. RCRA was a response to the reported three to four billion tons of toxic material haphazardly discarded each year. At the time of the act, Congress reported that hazardous waste generation was expected to increase at an annual rate of 8 percent per year [US Code Congressional and Administrative News, volume 5, 94th Congress, Second Session, 1976 Pages 6238 to 6354].

Congress assigned the implementation of the RCRA to the EPA. While EPA had been accustomed to regulating major environmental issues, it felt overwhelmed by the broad complexity of the new law. In an effort to quickly implement the new requirements, the EPA published interim rules for Treatment, Storage, and Disposal Facilities (TSDFs). On May 19, 1980, the EPA published a massive compendium of regulations to become effective on November 19 of that year [45 Fed. Reg. 33221]. In the preamble to section 264 of those rules, the EPA noted that proposed requirements for detailed waste analysis in the interim rules had provoked many comments in opposition to the presumably costly and redundant nature of the analyses.

Section 3006 of RCRA authorizes state hazardous waste programs. Section 3009, Retention of State Authority, says that a state may not impose requirements that are less stringent than those authorized under RCRA. The New Mexico Hazardous Waste Act says the state's hazardous waste program must be equivalent to and not more stringent than federal regulations adopted by the EPA pursuant to RCRA [Section 74-4-4(A)].

In reference to the RCRA program, many comments were addressed related to the requirement for annual retesting of waste streams. The EPA did agree that in some cases waste stream properties would not change over a year and allowed the owner/operator to test on an as-needed basis when the owner/operator thought there were changes in the waste. EPA dropped two additional requirements to 1) check for four physical and chemical properties stated in the proposed rule and 2) check each truckload of waste when the generator and owner/operator knew waste streams were uniform and unvarying among multiple truckloads of the same waste.

Instead, EPA required owner/operators to develop and follow a WAP. This plan would specify "...the tests to be used, and the frequency with which these tests [would] be conducted, to determine the identity of incoming waste managed at the facility" [Preamble to 40 CFR 264.13(b)]. EPA believed the requirement for developing and maintaining a WAP would encourage owner/operators to tailor their waste analysis

procedures to the types of wastes and techniques the facility used to manage those wastes. Additionally, the requirement provided EPA with a review mechanism to encourage owner/operators to conduct these thorough analyses. The WAP would be a separate, enforceable regulatory requirement.

Requirements for a WAP were codified at 40 CFR 264.13. They have been modified several times since 1980 to include some additional requirements, not all of which are of interest to this analysis. It is important to understand that these regulations were written with non-radioactive waste in mind. The hazards associated with exposure to radiation were not considered in the regulations but have been addressed in the *Joint NRC/EPA Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste*, 62 FR 62081, November 1997.

Waste Analysis Plan Requirements

The overall purpose of a waste analysis plan is to provide a process to comply with section (a) of the rule concerning general waste analysis. Section 264.13(a)(1) of the rule reads, in pertinent part, as follows:

Before an owner or operator treats, stores or disposes of any hazardous waste...he must obtain a detailed chemical and physical analysis of a representative sample of the wastes. At a minimum, the analysis must contain all the information which must be known to treat, store, or dispose of the waste in accordance with this part and part 268 of this chapter [40 CFR 264.13(a)(1)].

The WAP minimum requirements given in 40 CFR 264.13(b) require a TSDF owner/operator to describe procedures to be used to comply with paragraph (a) of the section. The required procedures must show that the owner/operator has sufficient detailed information to ensure that the waste management operations will be carried out safely.

At a minimum, the plan must include procedures: (1) to determine parameters for which each hazardous waste must be analyzed, rationale for selecting the parameters, and how

the analysis for these parameters will provide necessary information on waste properties; (2) test methods to be used; (3) the method that will be used to obtain a representative sample; (4) frequency of the analysis; and (5) waste analyses from off-site generators. Other requirements for the plan relate to certain types of facilities that are not pertinent to this analysis. These procedures are to ensure that the owner/operator can obtain the detailed information required to ensure the safety of the facility [40 CFR 264.13(b)(1)-(5)].

The owner/operator is required to obtain detailed chemical and physical information about the waste so that he might properly manage the waste. The AK, or waste knowledge "...is allowed by RCRA regulations to comply with the following requirements:

- To determine if a waste is characteristically hazardous (40 CFR 262.11(c)(2) or matches a RCRA listing in 40 CFR Part 261, Subpart D (40 CFR §262.11(a) and (b));
- To comply with the requirements to obtain a detailed chemical/physical analysis of a representative sample of the waste under 40 CFR §264.13(a)..." (*Joint NRC/EPA Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste*, 62 FR 62081, November 1997.)

EPA clearly states that the detailed analysis may include existing data such as process knowledge, published chemical abstracts, or other information developed by the generator and that adequate waste knowledge alone satisfies the requirements for characterization. The EPA specifically stated in its joint guidance with the NRC, that,

"Hazardous waste, including mixed waste, may be characterized by waste knowledge alone, by sampling and laboratory analysis, or a combination of waste knowledge, and sampling and analysis." (*Joint NRC/EPA Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste*, FR 62081, November 1997.)

The EPA also stated in the guidance that, "the use of waste knowledge alone may be the most appropriate method to characterize mixed waste streams where increased radiation

exposures are a concern.” (FR, Vol. 62, No. 224, Page 62082) The EPA only requires the owner or operator of a TSDF to perform a detailed physical and chemical analysis of waste in the case where, “[I]f the generator does not supply the information, and the owner or operator chooses to accept a hazardous waste, the owner or operator is responsible for obtaining the information required to comply with this section” as provided in 40 CFR §264.13(a). Otherwise, the AK information alone provided by the generator satisfies 40 CFR §264.13(a)(1).

With respect to WAPs, the EPA has issued at least three guides that are instructive. The most widely cited guide on waste analysis, “Waste Analysis at Facilities that Generate, Treat, Store and Dispose of Hazardous Wastes – A Guidance Manual,” was issued in 1994 [OSWER 9938.4.03, April 1994]. This guide, updated from the 1984 version, provided comprehensive information on the structure of a WAP. Section 1.5 of the guide, related to waste analysis, is particularly relevant to this discussion. In this section, EPA noted that the best and most defensible way to meet waste analysis requirements was to conduct waste sampling and laboratory analysis. However, when data existed to assist the TSDF owner/operator in obtaining information required to manage the waste, the owner/operator may use AK to meet all or part of the waste analysis requirements. AK was defined broadly to include process knowledge, waste analysis data from generators, and facility records that predated the effective date of the RCRA regulations [OSWER 1994, page 1-11].

When EPA republished their rules in 1980, they abandoned the idea that each truckload and shipment of waste must be analyzed for its chemical and physical properties. In its place, EPA required the TSDF owner/operator to analyze a “representative sample” of the waste. Representative sample was defined in 40 CFR 260.10 as follows:

Representative sample means a sample of a universe or whole (e.g., waste pile, lagoon, ground water), which can be expected to exhibit the average properties of the universe or whole.

EPA does not require the owner/operator to sample [confirm] each batch or container of waste received at the facility if there is reason to believe that the waste is uniform and non-varying between shipments. WIPP employs testing methods such as nondestructive examination or visual examination to satisfy the confirmatory requirements in 40 CFR §264.13(b). Through these examinations, WIPP confirms that the waste being shipped to the facility conforms to the information submitted by the generator and included on the manifest or shipping papers.

Performance-Based Standards and Miscellaneous Units

In the joint NRC/EPA guidance, EPA explains that the RCRA program functions under a performance-based measurement system. Under this system, the regulation and permit focus is on monitoring, data quality objectives, and specific information that must be gathered and documented by the permittee to demonstrate compliance objectives have been achieved. EPA said, "Any reliable method may be used to demonstrate that one can see the analytes of concern in the matrix of concern at the levels of concern." EPA stated their belief "...that the frequency of testing is best determined on a case-by-case basis by the permit writer" [62 FR 62084]. This reliance on performance-based permitting is not new to the mixed waste guidance.

The *Joint EPA/NRC Guidance* specifically states that,

"[u]nder PBMS (Performance Based Measurement Systems), the regulation and/or permit focus is on the question(s) to be answered by the monitoring, the degree of confidence (otherwise known as the Data Quality Objective (DQO)) or the measurement quality objective (MQO) that must be achieved by the permittee to have demonstrated compliance, and the specific data that must be gathered and documented by the permittee to demonstrate that the objectives were achieved."

Under a performance-based measurement system, DQOs related to mixed waste characterization can be met with AK alone provided that AK contains all of the necessary information and is verified by the TSDF.

Conclusions

Taken as a whole, the statutory and regulatory history of RCRA, coupled with EPA guidance related to mixed wastes, reveals a strong preponderance toward the use of AK as the preferred means of satisfying 40 CFR 264.13(a) requirements, particularly for mixed wastes. Where historical AK does not adequately satisfy the requirements, additional AK must be obtained by waste sampling and laboratory analysis performed by the generator, or the TSDF if necessary, to provide the necessary information about the waste that is required by 40 CFR 264.13(a).

When the AK requirements have been satisfied, EPA also requires testing a representative sample of the waste to confirm the information. Beginning in 1980, EPA specifically rejected detailed analysis of each shipment, certainly every container, of waste received at a management unit when both generator and owner/operator knew that the waste had not changed. The examination of a representative sample of a waste stream satisfies the requirement to verify the characterization information as required in 40 CFR 264.13(b). Representative sampling depends on a statistically valid sampling program. It does not mean the TSDF owner/operator must sample every shipment to the facility nor does it specify intrusive sampling if an equivalent method, i.e. radiography, is available to accomplish the same task of confirming the waste matrix.

Finally, as a miscellaneous unit, WIPP must meet environmental performance standards which are performance-based. There is great latitude to formulate a WAP that provides the owner/operator information that is required to make decisions about safe operation of the facility. There are no prescriptive requirements for sampling frequencies, methods or types. The regulations have left this strictly up to the permit writer's discretion.

In conclusion, there are no statutory or regulatory roadblocks that preclude WIPP from modifying the Hazardous Waste Facility Permit (HWFP) to allow the exclusive use of waste knowledge (coupled with examination of a representative subpopulation of the waste stream) to satisfy requirements for waste analysis plans. Federal guidance, available in the absence of codified characterization requirements for mixed waste,

further supports this position. The *Joint NRC/EPA Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste*, 62 FR 62081, emphasizes of the use of process knowledge alone, whenever possible, to perform waste characterization in order to avoid unnecessary exposures to radioactivity.

There is no statutory or regulatory basis for requiring the examination, sampling and analysis of 100 percent of the containers in every waste stream. The EPA does require the verification of characterization information by the examination or analysis of a representative sample, which may be satisfied by radiographic examination of a representative subpopulation of containers. The EPA and NRC recommend using available characterization methods that will provide the necessary information and minimize workers' exposure to ionizing radiation.